Global phosphorus scarcity and full-scale P-recovery techniques – a review

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Phosphorus is an essential element for all life on earth. However, natural phosphorus resources (phosphate rock) are depleting. This paper describes the current situation and a forecast for future phosphate production and reserves. The current depletion of phosphate reserves and the increasingly stringent discharge regulations have led to the development of various phosphorus (P) recovery techniques from wastewater. Existing full-scale P-recovery techniques from the liquid phase, from the sludge phase and from sludge ash are reviewed. Although the full-scale P-recovery techniques have been shown to be technologically feasible, the economical feasibility, legislation and national policies are the major reasons why these techniques are not yet operational worldwide.

Keywords: phosphorus, reserves, depletion, P-recovery techniques

1. Introduction

Phosphorus is a non-metal of the nitrogen group and is essential for all life on our planet. Elemental phosphorus has been known for about 350 years and exists in two major allotropes, namely white and red phosphorus. These allotropes have a great diversity of physical properties and chemical reactivity. The most common form is white phosphorus or tetraphosphorus (P_4), which has a tetrahedral structure and is highly reactive with air, while red phosphorus exists as polymeric chains (P_n) and is more stable (Pfitzner *et al.*, 2004). White phosphorus transforms to red phosphorus when exposed to sunlight, or by heating it in anoxic conditions to 250 °C. However, phosphorus is never found as a free element due to its high reactivity, but it is widely distributed in many minerals, mainly phosphates. These geological deposits of phosphate are called phosphate rock or phosphorite and are found all over the world. They can be divided into two main categories: sedimentary and igneous phosphate rock deposits. The latter are often low in grade and expensive to recover. The former deposits are more plentiful than the igneous rock deposits and they provide more than

80 % of the total world production of phosphate rock. The majority of today's global phosphate rock production is used in agricultural products and/or applications, mainly in fertilizers (Cisse and Mrabet, 2004). In addition, phosphorus is ubiquitous in all living organisms and accounts for around 2-4 % of the dry weight of most cells (Karl, 2000). It is the second most abundant mineral in the human body, only surpassed by calcium. It is mostly found in bones and teeth (biomineral hydroxyapatite). Moreover, it is a key player in fundamental biochemical reactions (Westheimer, 1987) involving genetic material (DNA, RNA) and energy transfer within the cell through the molecule adenosine triphosphate (ATP), and in structural support of organisms provided by membranes (phospholipids).

It can be concluded that phosphorus occupies a prominent role in modern life; the main objective of this paper is to investigate the current status of phosphorus availability, and potential techniques to recover phosphorus from waste streams in view of enhancing the availability. It is well known that the world phosphate reserves of high grade are being depleted nowadays due to the increasing demand (Steen, 1998). Thus, for a good understanding, the current situation and the future forecasting of the phosphate production and reserves will be described. Furthermore, the depletion of the phosphate reserves in combination with the fact that phosphorus is a non-renewable resource has led to the development of numerous techniques to recover phosphorus from various waste streams (Cordell *et al.*, 2009). An extensive overview of the existing variety of full-scale P-recovery techniques that may allow to increase the future availability of phosphorus will be given.

2. Depletion of phosphate reserves

2.1. Phosphorus and its use

Phosphorus is widely distributed in many minerals, but by far the most abundant family of minerals are apatites, with chemical formula $Ca_5(PO_4)_3(F,Cl,OH,Br)$. Apatites occur in four

forms of calcium phosphate depending on the element of largest share: hydroxyapatite, fluorapatite, chlorapatite, and bromapatite (Ward *et al.*, 1996). Fluorapatite as a mineral is the most common phosphate mineral and provides the most extensively mined deposits. In addition to apatite, phosphate rock contains impurities such as humic substances and heavy metals, especially cadmium, uranium and zinc. Typically, phosphate rock contains 30-40 % P_2O_5 (= 13-17.5 % P) (Schipper *et al.*, 2001). The phosphorus content of ore or fertilizer is often expressed as P_2O_5 due to the traditional gravimetric method to determine the phosphorus content in ores.

The phosphate-based products are used in numerous applications, which can be divided into two main categories: agricultural and non-agricultural applications. Most of the global phosphate production (approximately 95 %) is used in agricultural applications, mainly in the fertilizer industry, but also for the production of phosphorus-based pesticides and animal feed supplements. By far the most important use of phosphate rock is fertilizer. Up to 90 % of all mined phosphate rock is used to produce mineral fertilizers (Cisse and Mrabet, 2004). Phosphorus is one of the three main primary macronutrients, together with nitrogen and potassium, which are the basis of inorganic fertilizers. Nowadays, there is a strong increase of fertilizer demand due to the increasing world population, rising demand for high quality food and the use of plant derived biofuels. Since fertilizers are crucial for an efficient plant production, their lack can result in crop failure. Therefore, the importance of phosphorus cannot be underestimated. The most important mineral phosphate fertilizers and their chemical formulas as well as the phosphorus content are listed in Table 1.

Non-agricultural applications include the food industry, household applications, and other industrial applications. In the food industry, phosphate compounds are part of baking powders, and are present in bottled soft drinks to prevent bacterial growth and for buffering the pH. Phosphate-based products are also present in various household applications: high

grade detergents, cleaning agents, toothpastes and dental creams, etc. Moreover, phosphate is used in numerous industrial applications such as metal surface treatment, corrosion inhibition, flame retardants, etc. Despite the widespread use, these applications represent only a small part of the total consumption (≤ 5 %).

Table 1 Overview of typical phosphorus fertilizers (Data from Müller *et al.*, 2005).

Compound	**Acronym**	**Formula**	**Nutrient content (% P)**
Ordinary superphosphate	OSP	$Ca(H_2PO_4)_2 + CaSO_4$	8-9
Triple superphosphate	TSP	$Ca(H_2PO_4)_2$	19-20
Monoammonium phosphate	MAP	$NH_4H_2PO_4$	21-24
Diammonium phosphate	DAP	$(NH_4)_2HPO_4$	20-23

2.2. Current distribution of phosphate production and reserves

Currently, about 180-190 million tons of phosphate rock are mined globally each year (U.S. Geological Survey, 2012). The annual amount mined peaked in 1989, followed by a significant decrease over the next 10-15 years. This decrease is due to a lower application of inorganic fertilizer by most developed countries at that time: European Union, Japan, and North America. Moreover, there was also a strong reduction of fertilizer use in post-communist economies of the former Soviet Union (Smil, 2000). In recent years, there is again a strong increase in mining of phosphate rock, this time due to a strong increase in fertilizer demand in developing countries. The result is that the 1989 peak was surpassed in 2009, and the upward trend is estimated to continue. Future prospects will be discussed in the next section.

According to the U.S. Geological Survey (2012), the chief mining areas of phosphate rock are China, USA and Morocco. The largest sedimentary reserves of phosphate rock are found in northern Africa, China, the Middle East and the USA. Significant igneous reserves are found in Brazil, Canada, Russia, and South Africa. In addition, large deposits have been detected in the continental shelves in the Atlantic Ocean and the Pacific Ocean. However, the recovery of these deposits is considered to be expensive because until now one is still looking for an optimal and profitable technique for deep ocean mining. Table 2 shows the annual phosphate rock production for the most important countries worldwide for the years 2010 and 2011 (2011 is an estimation). The last column shows an estimation of the current reserves. From this table, it can be seen that Morocco and the Western Sahara contain an estimated 70 % of the remaining world phosphate reserves.

Figure 1 presents the consumption and supply of mined phosphate rock in the world. Despite its considerable reserves and large production, the United States consistently has to import phosphate rock. The import is necessary due to their lack of high-quality phosphate rock and the fact that U.S. companies export large quantities of phosphate fertilizers all over the world. Nearly all of these imports come from Morocco. In Asia, although the production level is high, the exceeding consumption leads to a need to import. Moreover, China currently protects its own reserves with export levies. This leads to Morocco being the most important producer. Of all the major global powers, Europe is the most dependent on the import of phosphate rock. Almost the entire stock must be imported from outside the continent.

Table 2 Global phosphorus production in 2010 and 2011 and current reserves (in 1000 metric tons) (Data from U.S. Geological Survey, 2012).

Country	**2010**	**2011**	**Reserves**
United States	25,800	28,400	1,400,000
Algeria	1,800	1,800	2,200,000
Australia	2,600	2,700	250,000
Brazil	5,700	6,200	310,000
Canada	700	1,000	2,000
China	68,000	72,000	3,700,000
Egypt	6,000	6,000	100,000
India	1,240	1,250	6,100
Iraq	-	-	5,800,000
Israel	3,140	3,200	180,000
Jordan	6,000	6,200	1,500,000
Morocco and Western Sahara	25,800	27,000	50,000,000
Peru	791	2,400	240,000
Russia	11,000	11,000	1,300,000
Senegal	950	950	180,000
South Africa	2,500	2,500	1,500,000
Syria	3,000	3,100	1,800,000
Togo	850	800	60,000
Tunisia	7,600	5,000	100,000
Other countries	6,400	7,400	500,000
World total	**181,000**	**191,000**	**71,000,000**

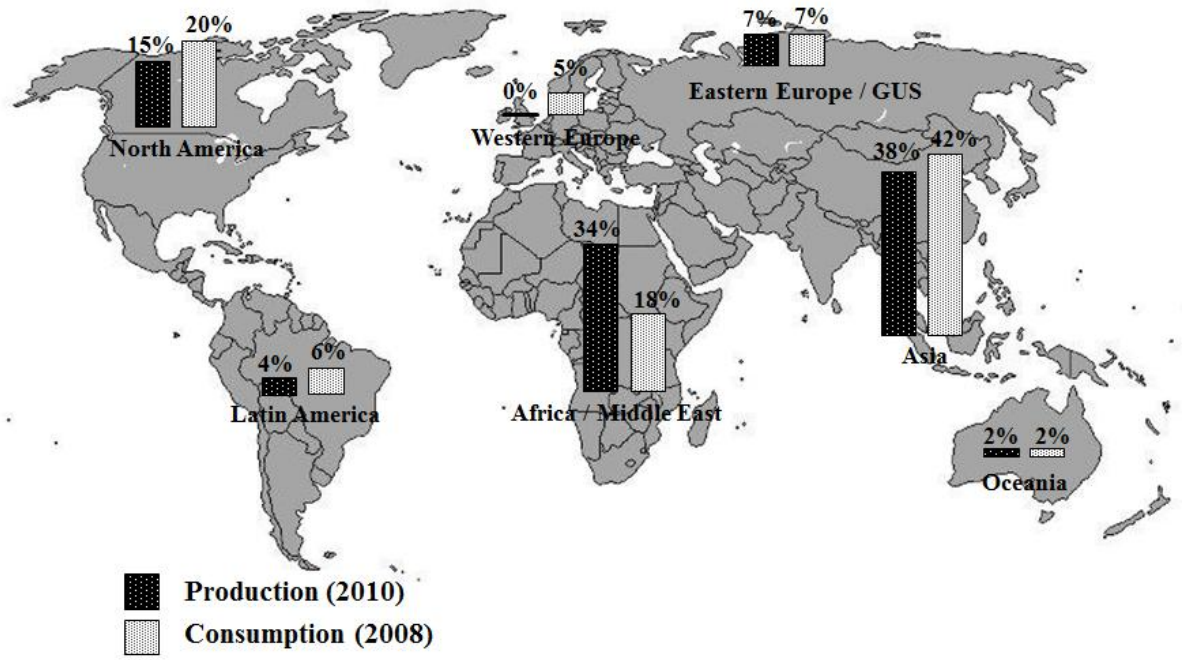

Figure 1 Global production and consumption of phosphorus (Data from U.S. Geological Survey, 2012; IFA, 2012).

2.3. Future demand for phosphorus

The demand for phosphorus is increasing globally, despite a downward trend in developed regions. This is due to the increasing population and global trends towards more meat- and dairy based diets, which are significantly more P intensive (Heffer and Prud'homme, 2009). Cordell *et al.* (2009) claimed that the rate of production of economically available phosphate reserves will peak between 2030 and 2040, after which demand would exceed supply, which in turn will lead to global phosphorus scarcity. At the current rate of mining, the current phosphate rock reserves would be fully depleted in around 372 years, using the data from Table 2. Since the production and demand are still increasing this period will presumably be less than 372 years. However, there is still a strong disagreement in the forecasts of how long the current phosphate rock reserves will last. Several studies claim that the depletion of the natural phosphorus reserves can be estimated to occur within a period of 100-400 years

(Günther, 1997; Cisse and Mrabet, 2004; Van Vuuren *et al.*, 2010). The large differences between the various studies can be explained by differences in the estimates in the peak production, use of different resource data and use of various calculation models.

The rapid depletion of high quality minerals is even more alarming. Mining an ore strongly depends on factors such as ore grade, impurities, cost-benefit ratio and accessibility. Low grade resources often contain high amounts of impurities such as aluminium, iron and magnesium and thus comprise a lower phosphate content. The most accessible and higher quality rocks tend to be mined first. As a consequence, the quality of phosphate rock is declining because the concentration of associated impurities (like carbonates and silicates) and heavy metals (like cadmium and uranium) is increasing (Heffer et al., 2006).

These negative expectations about the current phosphate reserves have an influence on the price of phosphate rock and its products. While demand continues to increase, the cost of mining phosphate rock is increasing due to the decline in quality and greater expense of extraction (for instance mining of deeper soil layers), refinement, transportation and environmental management. Predictions of the price development of phosphate rock have been performed by Van Vuuren *et al.* (2010) and by Horn and Sartorius (2009). Both analyses show that even without total depletion of the current reserves, it is very likely that the cost will significantly increase. An increase in the price will have an negative effect on the demand and the search for alternatives (P-recovery technologies) will be favoured. When the phosphate price increases, marginal deposits may become economically viable. In addition, alternative mining methods (mining of deeper soil layers) will be developed and new deposits will be opened, possibly in challenging environments (Van Vuuren *et al.*, 2010). In this situation the depletion of phosphorus will go slower.

Several factors such as the price of phosphate rock, the world population growth, the demand for food and the phosphate rock reserves determine the period when all phosphate

rock will be depleted. This makes it difficult to make a prediction of the exact period. However, all studies assume that at a given moment, there will be a depletion of naturally occurring phosphate rock, which means that 'doing nothing' is no sustainable long-term possibility.

3. Open phosphorus cycle and need for recovery

In the time of traditional societies (prior to industrialization) the phosphorus cycle was closed. However, due to modern human activities and associated industrialization, the phosphorus cycle has been broken and more phosphorus has been discharged into the natural water bodies from the land. As illustrated in Figure 2, phosphate rock is mined and used in both agricultural applications (mainly used as fertilizer) and industrial applications. Without P-recovery techniques, phosphorus enriched waste is produced by sewage treatment.

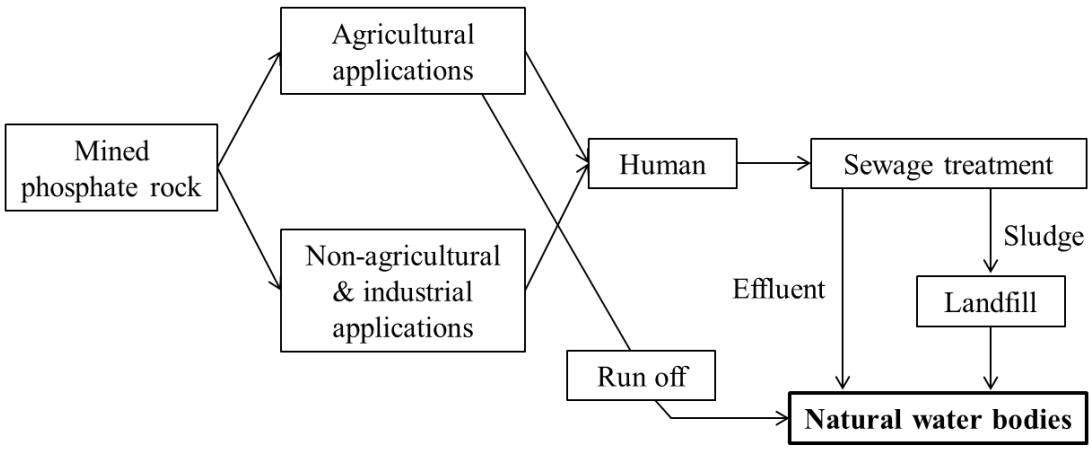

Figure 2 Open phosphorus cycle in modern society (Modified from CEEP, 2012a).

According to Cornel and Schaum (2009), an average of approximately 11% of the incoming phosphorus load is removed with the primary sludge during primary settlement (primary treatment step of sewage treatment). In biological wastewater treatment (activated sludge; secondary treatment step) approximately 20-30% of the incoming phosphorus load are

incorporated into the biomass and removed with the surplus sludge, even without specific phosphorus removal processes (Parsons and Smith, 2008). The disposal of phosphorus into the natural water bodies has a major impact on the aquatic ecosystem. This phenomenon, which is known as eutrophication, leads to a sharp decline in aquatic biodiversity, the loss of potable water resources, and contributes to the formation of oceanic dead zones (Dils *et al.*, 2001). Therefore, phosphate discharges have to be limited due to the increasingly stringent regulation to protect surface waters from eutrophication. Based on the permitted discharge concentrations of 1 $mg.L^{-1}$ P (10 000 – 100 000 Inhabitant Equivalent (IE)) or 2 $mg.L^{-1}$ P (> 100 000 IE) in Europe (Council Directive 91/271/EEC), approximately another 50% of the incoming phosphorus load has to be removed additionally.

In conventional wastewater treatment plants the remaining phosphorus is mainly eliminated by chemical precipitation with metal salts or by enhanced biological phosphorus removal (EBPR) (Tchobanoglous *et al.*, 2003) or a combination of both. In total, approximately 90% of the incoming phosphorus load is thus incorporated into the sewage sludge. With EBPR, phosphorus accumulating organisms (PAOs) incorporate phosphorus into cell biomass and the phosphorus is removed from the process by sludge wasting (waste activated sludge) (Tchobanoglous *et al.*, 2003). Chemical precipitation with metal salts can remove the phosphorus to low levels in the effluent. The commonly used chemicals are aluminum (Al(III)), ferric (Fe(III)) and calcium (Ca(II)). The chemicals can be added before the primary settling, during secondary treatment or as part of a tertiary treatment process (Parsons and Berry, 2004). However, large amounts of chemicals are required to obtain such low levels (1 or 2 $mg.L^{-1}$ P) , and large volumes of sludge are produced. Furthermore, metal phosphate salts, like iron or aluminium, cannot be reused in agriculture because the iron or aluminium phosphates are not available for plants under normal pH conditions. Due to the presence of iron or aluminium (which are added to precipitate phosphates) and the increasing

contamination of wastewater sludge with heavy metals and toxic organic substances, its application in agriculture has become increasingly unpopular or has been phased off completely (Satorius *et al.*, 2012). The sludge produced ends up in landfills, incinerators or in the sediments of canals and rivers (Mainstone *et al.*, 2000). The disposed phosphorus (in both liquid and solid state) finally ends up in the natural water bodies (such as aquifer, river, sea etc.). It is clear that this strategy accelerates the depletion of phosphorus.

In Figure 2, both sources (solid and liquid state) are regarded as waste streams, in which the focus lies on minimizing the cost of disposal. However, the phosphorus-containing waste enters the environment, causing phosphorus losses and eutrophication problems. Therefore, more sustainable techniques, such as phosphorus recovery techniques for both solid and liquid waste are important to close the phosphorus cycle in modern human society as shown in Figure 3.

From the literature review, it can be concluded that phosphate rock is becoming increasingly scarce and expensive. In addition, the phosphate discharges have to be limited due to economical and especially environmental impacts. Therefore, phosphorus needs to be recovered and reused from current waste streams. The implementation of an appropriate P-recovery strategy is of crucial importance. Nowadays, there are numerous P-recovery techniques and processes, although they are not yet widely used (Cordell *et al.*, 2011). In the next section the P-recovery products that can be obtained from P-recovery processes and of the existing variety of full-scale P-recovery techniques and their final products from various waste streams are reviewed.

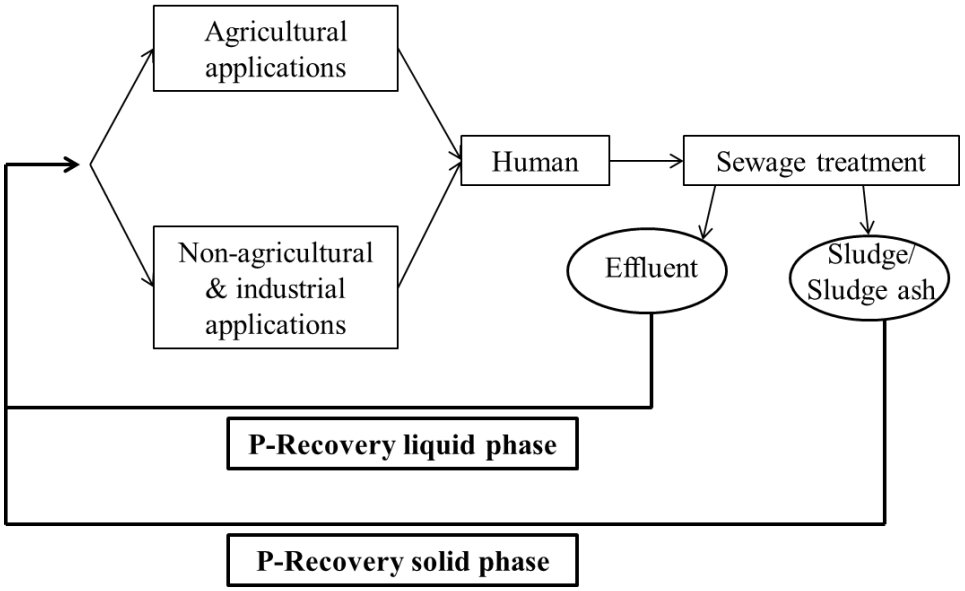

Figure 3 Closed phosphorus cycle including a recovery process (Modified from CEEP, 2012a).

4. Full scale technologies in P-recovery for municipal and industrial wastewater

4.1. Phosphorus recovery in practice

Phosphate recovery techniques developed for industrial or municipal wastewater treatment can be applied at various points in the treatment process. Phosphate can be recovered from the liquid phase (1), from the sludge phase (2) and from mono-incinerated (sludge is incinerated separately from other wastes) sludge ash (3) (Cornel and Schaum, 2009). As already stated in part 3, approximately 90% of the incoming phosphorus load, from the wastewater, is incorporated into the sewage sludge. The phosphorus recovery rate from the liquid phase can reach 40 to 50% at most, while recovery rates from sewage sludge and sewage sludge ash can reach up to 90% (Cornel and Schaum, 2009). Figure 4 shows the possible locations for phosphate recovery.

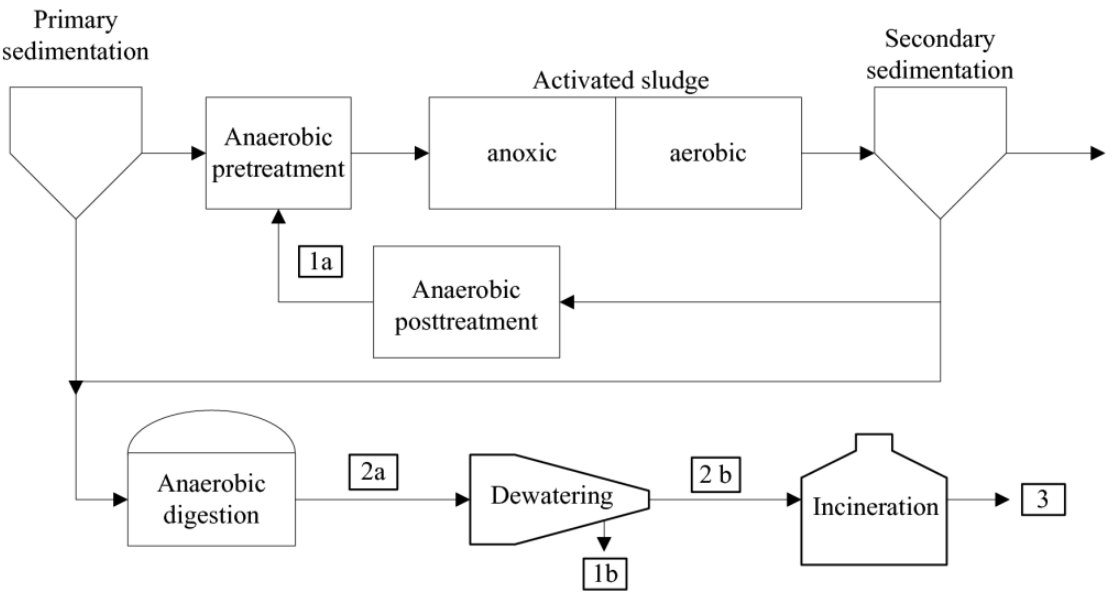

Figure 4 Possible locations for phosphorus recovery (modified from Cornel and Schaum 2009). 1a: side stream after anaerobic treatment; 1b: dewatering unit after anaerobic digestion; 2a: sludge from the digestor before dewatering; 2b: sludge from the digester after dewatering; 3: sewage sludge ash after incineration.

The economically feasible recovery requires a liquid phase containing 50-60 $mg.L^{-1}$ of PO_4-P (Cornel and Schaum, 2009). The phosphorus recovery methods from the liquid phase are usually located in a wastewater treatment plant (WWTP) with a biological phosphorus removal process since the polyphosphates stored in the bacterial cells are partly released again under anaerobic conditions, which significantly increases the phosphate content in the sludge system. Therefore, the concentrated side streams after the anaerobic treatment (1a) or the dewatering unit after anaerobic digestion (1b) are the best options for phosphorus recovery. The phosphorus content in wastewater treatment plants with bio-P removal and anaerobic digestion can be 75 to 300 $mg.L^{-1}$ PO_4-P (Garcia *et al.*, 2012). Phosphate recovery from the sludge phase which contains phosphorous in chemically and/or biologically bound form, includes recovery from the digester sludge before (2a) and after (2b) the dewatering unit. In

the third option the phosphorus is recuperated from the sewage sludge ash (3) in which it is in the most concentrated form. The decrease in volume results in decreased transporting and land filling costs. Recovery of phosphate from the sludge ash, together with sludge ash from other WWTPs, generally takes place at an external and central location.

In recent years phosphorus (P) recovery from municipal and industrial wastewaters has drawn much attention of the water industry, the phosphorus industry and the policy-makers (Driver *et al.*, 1999; Schipper *et al.*, 2001; Roeleveld *et al.*, 2004). The substantial difference between the traditional P removal and P-recovery from wastewater is that P removal aims at obtaining a P free effluent by transferring P to sludge with chemical and biological processes. P-recovery, on the other hand, aims at a P-containing product that can be reused either in agriculture or in P-industry. As discussed in Figure 4, phosphorus can be recovered from wastewater, sewage sludge and sewage sludge ash and a number of full scale techniques are already operational. Currently, most techniques aim at recovering phosphate from dewatering reject streams. These techniques recover phosphorus from the wastewater by feeding the phosphorus rich wastewater into a precipitation/crystallization tank which is either mixed or in fluidized state. Calcium or magnesium salts and where needed seed crystals are added to recover phosphate as calcium phosphate or struvite. The low TSS (Total Suspended Solids) concentration in the wastewater stream makes it relatively easy to separate phosphate precipitates from the wastewater. However, these methods do not prevent scaling problems in the sludge line before the precipitation/crystallization tank. When however phosphate is recovered from the sewage sludge directly after anaerobic digestion, the risk for scaling problems in the remainder of the sludge line can be significantly reduced. It also improves the dewatering properties of the sludge and is therefore an important economic incentive.

Phosphorus can be recovered from sewage sludge and sewage sludge ash by a wet chemical or a thermal technology. At the moment one wet chemical technology and two thermal techniques are working at full scale. Several others are under development (Lodder and Meulenkamp, 2011). Table 3 and Table 4 give an overview of the full scale techniques that will be discussed in this part.

Table 3 Overview of the flow for the full scale phosphate recovery processes for municipal and industrial wastewater

Full-scale processes	**Used technology and reactor type**	**Input flow (m^3/d)**	**Influent P concentration (mg/L)**	**Final product**	**Production (ton final product.d^{-1})**	**Removal Efficiency (wt %)**
ANPHOS®	P recovery from wastewater in a batch reactor	100/4800	580/58	Struvite	0.45/2	80-90
PHOSPAQ™	P recovery from wastewater in a CSTR	2400-3600	60-65	Struvite	0.8-1.2	80
NuReSys®	P recovery from wastewater/sludge in a CSTR	1920-2880	60-150	Struvite Biostru®	1.43-1.58	85
Phosnix	P recovery from wastewater in a fluidized bed	650	100-110	Struvite	0.50-0.55	90
Ostara Pearl™	P recovery from wastewater in a fluidized bed	500	100-900	Struvite Crystal Green®	0.50-4	85
Crystalactor®	P recovery from wastewater in a fluidized bed	100-150	60-80	Calcium phosphate	0.55-0.82	70-80
Airprex	P recovery from sewage sludge in a CSTR	1680-2000	150-250	Struvite	1-2.5	80-90
Seaborne	Wet chemical P recovery from sewage sludge in a CSTR	110	600	Struvite	0.58	~ 90
Thermphos	Thermal P recovery from sewage ash in a furnace	11000 ton ash/year	0.09 ton P/ton ash	P_4	11	> 90
Ash Dec®	Thermal P recovery from sewage ash in a furnace	7 ton/d	0.046 ton P/ton Ash	Calcined P fertilizer Phoskraft®	-	> 90

Table 4 Overview (Developers, influent type, chemicals, locations and market) of the full scale phosphate recovery processes for municipal and industrial wastewater

Full-scale processes	Developer	Influent type	Chemicals	Location(s) - Country (number of installations)	Market
ANPHOS®	Colsen bv	Anaerobic effluent/ Rejection water	MgO	The Netherlands (4)	Exported to Germany, mixed up with other fertilizers
PHOSPAQ™	Paques bv	Rejection water	MgO	The Netherlands (2)	Exported to Germany, mixed up with other fertilizers
NuReSys®	Akwadok bvba	Anaerobic digestion effluent/ Digested sludge	$MgCl_2$, NaOH	Germany (1) Belgium (2)	Exported to wine grower in France, mixed with compost
Phosnix	Unitika Ltd.	Wastewater after digestion or sludge treatment	NaOH, $Mg(OH)_2$	Japan (2)	Sold to fertilizer companies
Ostara Pearl™	University of British Colombia/ Ostara	Sludge dewatering liquid	$MgCl_2$, NaOH	USA (4)	Used as slow release fertilizer at golf courses and municipal lawns
Crystalactor®	DHV Water bv	Anaerobic effluent	Sand, NaOH, H_2SO_4, $Ca(OH)_2$	The Netherlands (2-closed)	Secondary raw material at Thermphos
Airprex	Berliner Wasserbetriebe	Digested sludge/ sludge liquor	$MgCl_2$, Flocculent	Germany (2) The Netherlands (1)	Fertilizer industry

Table 4 Overview (Developers, influent type, chemicals, locations and market) of the full scale phosphate recovery processes for municipal and industrial wastewater (continued).

Full-scale processes	**Developer**	**Influent type**	**Chemicals**	**Location(s) - Country (number of installations)**	**Market**
Seaborne	Seaborne Environmental Research Laboratory	Digested sludge	H_2SO_4, Na_2S, NaOH, MgO, Flocculent	Germany (1)	Reused as fertilizer in agriculture
Thermphos	Thermphos	Sludge ash		The Netherlands (1)	Production of phosphoric acid, phosphonates and phosphorus derivates
Ash Dec®	Ash Dec (Outotec)	Sludge ash	$MgCl_2$, $CaCl_2$	Austria (1)	Reused as fertilizer on pasture and cropland

4.2. Final products from P-recovery processes (municipal and industrial wastewater)

It is commonly considered that crystallization processes can recover P from the liquid phase either as calcium phosphates that are similar to phosphate rocks, or as magnesium ammonium phosphate hexahydrate (also known as struvite), which is a slow release fertilizer. Another form of struvite is K-struvite ($KMgPO_4.6H_2O$). K-struvite has a similar structure as struvite ($MgNH_4PO_4.6H_2O$); the only difference is the replacement of NH_4^+ into a smaller K^+ ion. Phosphorus can also be recovered from sludge or sludge ash as struvite or calcinated phosphate. Another possibility to re-use the phosphorus from sewage sludge ash is as a partial substitute for phosphate rock in the production process of white phosphorus (Schipper *et al.*, 2001). In this way the phosphorus in the sludge ash is processed to white phosphorus.

4.2.1. Calcium phosphate

Calcium phosphate precipitation is very complex and involves various parameters. In particular, it depends on calcium and phosphate ions concentrations, as well as on supersaturation, ionic strength, temperature, ion types, pH but also on time (solid–solid transformation) (Song *et al.*, 2002; Montastruc *et al.*, 2003). The different forms of crystallized calcium phosphate are presented in Table 5 (Montastruc *et al.*, 2003). Which specific crystalline calcium phosphate forms will precipitate depends mostly on pH and kinetics. The phase predicted to be stable is dicalcium phosphate dihydrate (DCPD; $CaHPO_4.2H_2O$) at acidic pH around 5, octacalcium phosphate (OCP; $Ca_8H(PO_4)_6.5H_2O$) at pH around 6 and hydroxyapatite (HAP; $Ca_5(PO_4)_3OH$) at pH of 7 and above (Seckler *et al.*, 1996). However, the precipitated phase will most likely transform into the thermodynamically more stable HAP (Kibalczyc, 1989).

Table 5 Different forms of calcium phosphate (Montastruc *et al.*, 2003).

Name	Formula
Dicalcium phosphate dihydrate (DCPD)	$CaHPO_4.2H_2O$
Dicalcium phosphate anhydrate (DCPA)	$CaHPO_4$
Octocalcium phosphate (OCP)	$Ca_8H(PO_4)_6.5H_2O$
Tricalcium phosphate (TCP)	$Ca_3(PO_4)_2$
Amorphous calcium phosphate (ACP)	$Ca_3(PO_4)_2$
Hydroxyapatite (HAP)	$Ca_{10}(PO_4)_6(OH)_2$

In practice the kinetics of calcium phosphate precipitation play a more important role than thermodynamic equilibrium considerations. In most cases, spontaneous precipitation of calcium phosphate from the solution does not occur at all or only with very high oversaturation (Cornel and Schaum, 2009). It is also believed that the effects of some inhibitors account for this phenomenon. Carbonate and ammonium alkalinity are the most important chemical components in wastewater contributing to the buffering capacity in the alkaline pH range. When for instance calcium hydroxide is added to wastewater, to increase the pH for the precipitation of calcium phosphate, the hydroxide reacts with the existing bicarbonate to form carbonate, with ammonium to form ammonia (NH_3), and with phosphate to form phosphate containing precipitates (Vanotti and Szogi, 2009). Using calcium hydroxide thus leads to the following reactions:

$$Ca(OH)_2 + Ca(HCO_3)_2 \rightarrow 2\ CaCO_3 + 2\ H_2O \quad (1)$$

$$5\ Ca^{2+} + 4\ OH^- + 3\ HPO_4^- \rightarrow Ca_5OH(PO_4)_3 + 3\ H_2O \quad (2)$$

The reaction in Equation 1 is complete at pH $\leq$ 9.5, while that of Equation 2 starts at pH > 7.0, but is very slow below pH 9.0. As the pH value of the wastewater increases beyond 9.0,

excess Ca ions will react with the phosphate, to precipitate as HAP (Equation 2). In wastewater that contains high ammonium concentrations, large amounts of lime are required to elevate the pH to the required values since ammonium reaction tends to neutralize the hydroxyl ions according to Equation 3:

$$Ca(OH)_2 + 2NH_4^+ \rightarrow 2\ NH_3 + Ca^{2+} + 2\ H_2O \quad (3)$$

Song *et al.* (2002) found that at pH 8 the precipitation rate of phosphate was significantly retarded by carbonate and the corresponding precipitation efficiency also decreased, but at pH values greater or equal to 9 the effect of carbonate on the precipitation of phosphate was very small. This indicated that carbonate decreased the precipitation rate of calcium phosphate, but the solution pH value was still a key factor influencing the precipitation process. The effect of carbonate on the precipitation of phosphate is attributed to the formation of ion pairs between carbonate and calcium and the decrease of free calcium ions. This results in the decrease of the thermodynamic driving force for the precipitation of calcium phosphate, although this competing effect was not so obvious at pH larger than or equal to 9. Carbonate may be co-precipitated with phosphate from solution, especially at pH 9-11, and this will decrease the relative phosphorus content of the precipitate. Hence lime requirements for the precipitation of calcium phosphate are less independent of phosphate concentration, but are more related to wastewater alkalinity. The increase of both the solution pH value and the Ca/P ratio are two approaches to overcome negative influence of carbonate on the precipitation of phosphate.

Because recovered calcium phosphate is the effective composition of phosphate rock, it can be readily accepted by the phosphate industry if it is recovered in a suitable physical form (Driver *et al.*, 1999).

4.2.2. Struvite

In 1937, whilst studying digestion Rawn et al. found crystalline material identified as struvite in the digested sludge supernatant pipes (Rawn et al., 1937). Problems with struvite formation were again highlighted in 1963 at the Hyperion wastewater treatment plant where struvite crystal growth in a pipeline reduced the diameter from twelve to six inches (Borgerding, 1972). Since EBPR has been implemented in advanced biological nutrient removal (BNR), an extensive number of examples of struvite deposition and its associated problems have been reported (Doyle and Parsons, 2002). Micro-organisms that can take up phosphate in excess of their nutrient requirement, release this excess phosphate in anaerobic conditions, such as sludge digesters or the anaerobic compartments of advanced BNR plants. This may lead to precipitation and scaling in pipes that increase operation and maintenance costs. Areas of a wastewater treatment plant affected most by struvite deposition are places where there is an increase in turbulence such as pumps, aerators and pipe bends (Borgerding, 1972). The hypothesis is that turbulence causes a decrease in pressure resulting in the release of carbon dioxide (CO_2) and an associated rise in pH (Borgerding, 1972). Primarily struvite precipitation was thus considered as a problem (Borgerding, 1972; Doyle *et al.*, 2003). Nevertheless, the fertilizer potential of struvite has led wastewater companies and scientists to study its recovery (de-Bashan and Bashan, 2004; Meesschaert *et al.*, 2007). The success of struvite crystallization is governed by various parameters. Among the ones known to be particularly important are pH, magnesium concentration, presence of foreign ions and retention time. Struvite, or magnesium ammonium phosphate hexahydrate ($MgNH_4PO_4.6H_2O$) precipitates in a 1:1:1 molar ratio following the general equation 4 (with n = 0, 1, or 2) (Le Corre *et al.*, 2009):

$$Mg^{2+} + NH_4^{+} + H_nPO_4^{n-3} + 6\ H_2O \rightarrow MgNH_4PO_4.6H_2O + n\ H^{+} \quad (4)$$

In most sewage treatment applications magnesium is the limiting element, hence this is

added to the process as $MgCl_2$ or MgO. The saturation point of a solution is strongly influenced by pH, hence if the feed stream does not have sufficient alkalinity, sodium hydroxide is added and/or CO_2 is stripped from the solution. Both magnesium sources have advantages and disadvantages. The advantage of the addition of MgO is that it can be simultaneously used for pH adjustment and as magnesium source. On the other hand, MgO has a very low solubility. For this reason, it is added as a slurry rather than as a solution. This slow dissolution can be seen as a disadvantage, since a higher volume of the reaction zone or a higher retention time is needed and the addition of a slurry can give difficulties (e.g., blockage of pipes).

The recovered phosphate can be reused as a fertilizer, either directly or after processing by fertilizer industries. For the direct use as a fertilizer, the produced struvite has to be certified and recognized as a fertilizer. In Europe the recognition of fertilizers is determined by the EU Regulation 2003/2003 which contains a list of approved fertilizers, with the method of preparation and minimum contents of nutrients. If fertilizer products are in agreement with the EU-regulations, they have the EC-fertilizer status and they can be freely transported and delivered within EU member states. Struvite is not included in the list of approved fertilizers and thus it is seen as a waste product. Besides the EU directive 2003/2003 there are also national fertilizer ordinances of each member state. Each member state can recognize it as a fertilizer and give permission to transport it as a fertilizer and thus not as a waste (see 4.3.1 and 4.3.2).

In America, the produced struvite must meet the fertilizer registration requirements of the State where it is distributed.

4.2.3. White phosphorus (P_4), phosphoric acid and phosphate salts

To avoid wasting of phosphate available in waste streams from e.g., agriculture, sewage

treatment and industrial side streams in landfills, and to counteract the depletion of natural phosphate sources, routes for reuse are explored. One possibility is to replace phosphate rock by recycled materials (e.g., calcium phosphate, sewage sludge ash) in the electrothermal production of white phosphorus (Schipper *et al.*, 2001). The white phosphorus can then be further processed to high quality phosphoric acid and other phosphorus compounds. Phosphoric acid obtained via white phosphorus is the main source of phosphates used in detergents and other non-fertilizer applications.

4.2.4. Calcined phosphate fertilizers

Calcined phosphate fertilizers can be obtained from sewage sludge ash after a thermal decontamination (1000 °C) which is comparable to calcination (Hermann, 2012b). Calcined phosphates perform particularly well on soils with pH-values below pH 7. On soils with pH 6 and lower, they usually outperform water soluble, traditional phosphate fertilizers. Their characteristics are close to the well proven Thomas phosphate ($Ca_5(PO_4)_2SiO_2$) that used to be a by-product from steel production (Hermann, 2012b).

4.3. Phosphorus recovery from wastewater in mixed tanks

4.3.1. PHOSPAQ™ and ANPHOS®

Both the PHOSPAQ™ and ANPHOS® processes are developed in the Netherlands for the precipitation of struvite. The PHOSPAQ™ process, developed by Paques, takes place in one aerated CSTR (Continuous Stirred Tank Reactor). As a result of aeration, the pH increases by CO_2 stripping and provides mixing. Additionally, magnesium oxide is added to the reactor to remove phosphate as struvite at a pH of 8.2 to 8.3. A patented separator system at the top of the reactor is applied to retain the struvite into the system (Driessen *et al.*, 2009). The struvite is harvested from the bottom of the reactor and transferred into a container by means of a

screw press (Driessen *et al.*, 2009). The dry weight of the harvested struvite is around 75% and the crystals have an average size of around 0.7 mm (Driessen *et al.*, 2009).

Since 2006, the PHOSPAQ™ process is successfully applied at full scale by *Waterstromen* in Olburgen (the Netherlands) for the combined treatment of the anaerobic wastewater from an Upflow Anaerobic Sludge Blanket (UASB) reactor of the potato processing plant Aviko bv and the reject water from a sludge digester of a municipal wastewater treatment plant. The installation produces 1.2 ton of struvite per day (Driessen *et al.*, 2009; Abma *et al.*, 2010). In 2008, Waterstromen exploited a second full scale plant in Lomm (the Netherlands) treating the UASB effluent of a potato processing plant, producing 800 kg struvite per day (Rogalla, 2010). The average phosphate removal efficiency is about 80%. (Driessen, 2009).

The ANPHOS® process is developed by Colsen and is operated in batch in two separate reactors (Lodder and Meulenkamp, 2011). In the first reactor, the wastewater is aerated, which results in a pH increase due to CO_2 stripping. In the second tank, magnesium oxide is added to the wastewater to recover phosphate as struvite. After the reaction the struvite is precipitated, dewatered and dried (Lodder and Meulenkamp, 2011).

The ANPHOS® technology has been first implemented on a full scale at the wastewater treatment plant of a potato processing company at the Kruiningen (the Netherlands) site of Lamb-Weston/Meijer (LWM). The installation is placed in between the anaerobic treatment and aerobic treatment of the wastewater treatment plant (Brekelmans, 2008) and is able to produce 2 tons of struvite per day (Brekelmans, 2005). Other full scale installation were built for another factory of LWM in Bergen op Zoom (the Netherlands) (Mangus, 2010), a potato processing company Peka Kroef in Odiliapeel (The Netherlands) (Brekelmans and Versteeg, 2008) and a sewage treatment plant of Land van Cuijk (The Netherlands) for the treatment of rejection water (Colsen, 2012). The ANPHOS® process is

capable of removing 80-90% of the phosphate.

The struvite that is obtained during these processes are fine crystals that have the structure of sand. The struvite was first classified as a secondary raw material and exported as 'waste' to Germany where it is used as raw material for the production of fertilizers or mixed with other fertilizers to obtain a good nutrient content (Colsen, 2011; Haarhuis, 2011). From 2010 on, struvite obtained from the potato processing companies was recognized as struvite (magnesium ammonium phosphate) by a change in the national legislation of fertilizers (Haarhuis, 2011) in the Netherlands. In this way the product can be sold as struvite and not as a waste product, as it was the case at the start up of the process.

4.3.2. NuReSys®

NuReSys® stands for Nutrient Recycle System and is developed by the Belgian company Akwadok and is operated in two reactors. Figure 5 shows a schematic overview of the technology in which the anaerobic effluent of a WWTP is treated (Moerman et al., 2009).

The NuReSys® process differs from the ANPHOS® process since it is operated in continuous mode instead of batch at a lower residence time. Another difference with the ANPHOS® process is the use of $MgCl_2$ as a magnesium source and the addition of a 29 % NaOH solution to the crystallization reactor instead of using MgO. The crystallization tank is equipped with a simple blade impeller and a specific developed and fully automated control algorithm ensures an optimal pH (8-8.5), reagent dosing and varying mixing intensity. In this way the growth of novel crystalline matter upon existing crystals occurs and prevents unwanted impeller or reactor scaling. The struvite pellets formed are removed by intermittent purging (Moerman et al., 2009).

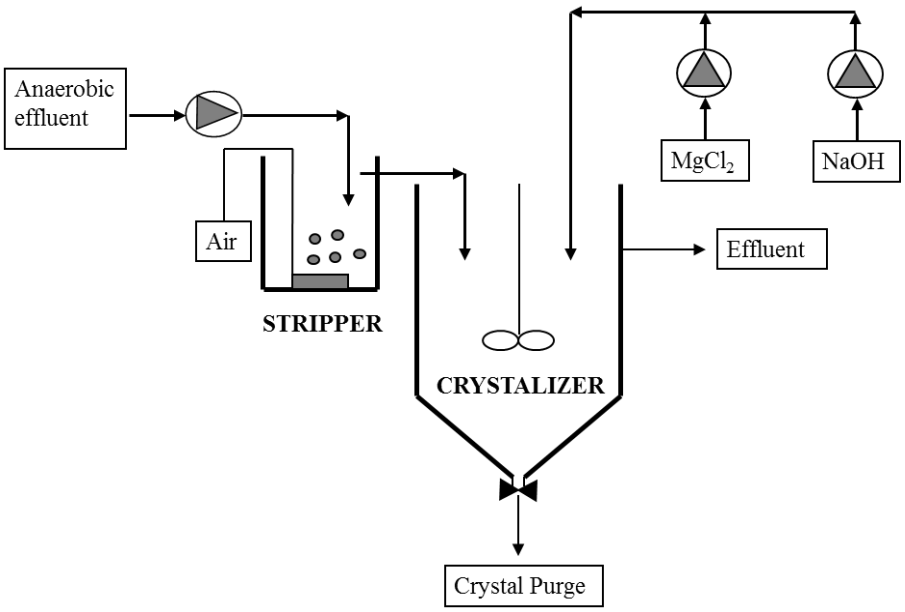

Figure 5 Schematic overview of the NuReSys® process (modified from Moerman *et al.*, 2009).

A first plant, with a capacity of 1580 kg struvite.day^{-1}, was taken into operation mid 2006 in Northern Germany by a dairy processing company. A 85 % removal of the phosphate is obtained during this process. The struvite produced has been accredited for reuse in agriculture **(**Moerman, 2012). A second full scale installation was implemented in 2008 at Agristo NV, a potato processing company located at Harelbeke (Belgium). This unit has a 1425 kg struvite.day^{-1} capacity. An average of 85% phosphate removal is also obtained at this site. A third full scale installation was installed in another potato processing company, Clarebout Potatoes NV in Nieuwkerke (Belgium).

The struvite has been identified as 100% struvite by XRD analysis and does compile with local (Belgium) directives defining required composition for reuse (BIOSTRU®) (Moerman, 2012). This BIOSTRU® may be used as a fertilizer or as a soil conditioner. In practice, a part of the final product is exported to a wine grower in France. Another part of the produced struvite is mixed up with compost (Moerman, 2012).

4.4. Phosphorus recovery from wastewater in fluidized bed reactors

4.4.1. Phosnix

The Phosnix process was developed in Japan by Unitika Ltd Environmental and Engineering Div. The Phosnix process is a side stream process that enables effective phosphate removal and recovery from the digester wastewater of the sludge treatment process in the sewage treatment plant as granulated struvite (Ueno and Fuji, 2001; Nawa, 2009). Figure 6 shows a schematic overview of the process. The wastewater is fed into the bottom of a fluidized bed reactor. The column contains a bed of granulated struvite which acts as a seed material for crystal growth. Magnesium hydroxide is added in a magnesium to phosphate ratio of 1:1 and the pH is adjusted to 8.2 – 8.8 with the addition of sodium hydroxide and by air stripping (Ueno and Fuji, 2001). A crystal retention time of 10 days allows the growth of pellets between 0.5 – 1.0 mm in size, after which they are purged from the bottom of the reactor column. Fine granules of struvite in the separated liquid are returned to the reaction column to provide new seed material in order to assure the continuity of the process (Ueno and Fuji, 2001; Ueno, 2004). The larger pellets are fed into a hopper (Figure 6) where the water content is reduced to less than 10%. Since 2001, two full scale struvite recovery plants (Ueno, 2004) are operational in Japanese sewage treatment works: one at the Fukuoka City West Waste Water Treatment Centre and the other at Shimane Perfecture Lake Shinji East Clean Centre. A removal efficiency of 90 % is obtained and the full scale reactors produce between 500 – 550 kg d^{-1} of struvite (Ueno and Fuji, 2001).

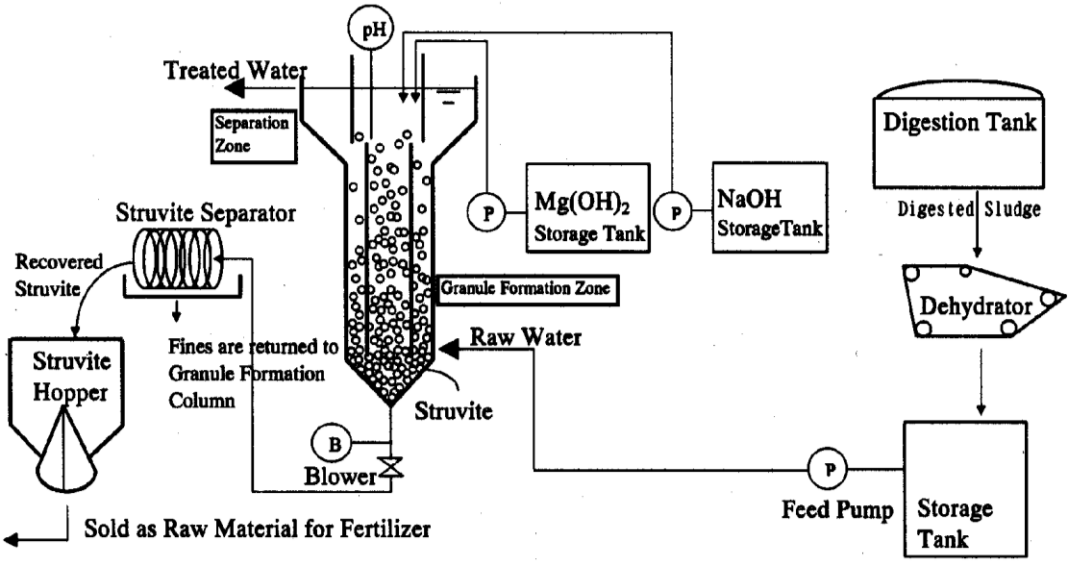

Figure 6 Schematic overview of the Phosnix process (Ueno and Fuji, 2001).

The struvite obtained was registered as a fertilizer in the category of 'High Performance Complex Fertilizers'; Fuku-MAP21 in July 1994 (Ueno, 2004). The recovered struvite is sold to fertilizer companies as raw material for chemical fertilizers (Ueno, 2004). The fertilizer companies buying the produced struvite do not use it as such but mix it with other inorganic and organic materials and adjust the proportion of nitrogen, phosphorus and potassium (Ueno, 2004). The produced fertilizers are widely used on paddy rice, vegetables and flowers; in particular it is claimed to significantly improve the taste of paddy rice (Ueno and Fuji, 2001).

4.4.2. Pearl™ and Wasstrip®

The Ostara Pearl™ process was developed in the University of British Columbia (Canada), and holds an U.S. Patent (Koch *et al.*, 2009). The process recovers struvite from the sludge liquor of an anaerobic digester, coming from a WWTP with biological phosphorus removal. The technology is based on controlled chemical crystallization in an up-flow fluidized bed

reactor with multiple reactive zones of increasing diameters, as shown in Figure 7 (Britton *et al.*, 2009). The process has the advantage of allowing large struvite pellets from 1.5 to 4.5 mm in diameter to be kept in suspension in the bottom of the reactor without washing out fine crystal nuclei from the top of the reactor (Lodder and Meulenkamp, 2011). It also provides better particle size classification than a typical single diameter fluidized bed reactor, thus allowing selective harvesting of product particles based on size. The high fluid velocity in the bottom of the reactor also results in the washout of residual sludge solids, and therefore a more pure struvite product free of organic material and pathogens is obtained (Britton *et al.*, 2009). Struvite crystallization is controlled by a combination of magnesium dose, pH control and by means of a treated effluent recycle (Koch *et al.*, 2009). The chemicals used for precipitation and the pH adjustment are $MgCl_2$ and NaOH, respectively. Pearl™ typically removes 85-90% of the phosphorus from the sludge dewatering liquid. The struvite production rate is 500 $kg.d^{-1}$.

The Ostara Group markets the final product struvite under the name Crystal Green® (N-P-K: 5-28-0 + 10% Mg) which is used as slow release fertilizer at golf courses and municipal lawns (Britton *et al.*, 2009). Currently, four full-scale plants have been implemented in the USA. The first industrial scale reactor opened in Edmonton, Canada in May 2007. Other reactors are located in the U.S. in Portland (Durham, Oregon), Suffolk (Virginia) and the City of York (Pennsylvania) (Lodder and Meulenkamp, 2011).

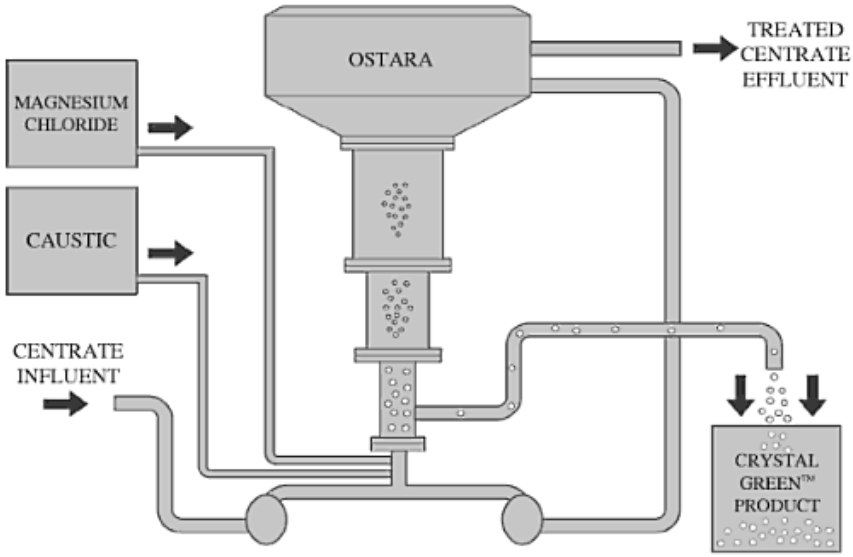

Figure 7 Schematic overview of the Pearl™ technology (Britton, 2009).

To further improve the performance of the process, the Ostara's Pearl™ process can be combined with the WASSTRIP™ (Baur, 2009) process developed by Clean Water Services, a water resource management utility in the Tualatin River Watershed at Durham, Oregon. WASSTRIP™ stands for Waste Activated Sludge STRIPping and is designed to remove internal phosphorus. The excess activated sludge or waste activated sludge of the wastewater treatment is sent to the anaerobic reactor where phosphorus and magnesium are released (stripped) by the micro-organisms as a consequence of endogenous respiration and fermentation. The resulting waste activated sludge is then sent to a thickening device and the resultant liquid, having enhanced phosphorus and magnesium are sent to the struvite reactor. The thickened waste activated sludge with reduced phosphorus and magnesium levels is finally sent to the anaerobic digester. This combination of the WASSTRIP™ and the Pearl™ process results in a higher struvite production and prevents scaling in the digester and the dewatering apparatus. In April 2011, the WASSTRIP™ process was implemented in the Durham WWTP (Schauer, 2012).

4.4.3. Crystalactor®

The Crystalactor® was originally developed in the early 1980's by the Dutch consultancy and engineering company DHV to remove calcium (hardness) from drinking water. Soon, the technology was used to remove several other components, such as phosphate and heavy metals from process water, drinking water and wastewater streams (Giesen and van der Molen, 1996).

EBPR is used to concentrate the phosphate in a side stream, which is then treated in the Crystalactor®. The phosphate rich flow contains 60 – 80 $mg.L^{-1}$ PO_4-P and is collected in buffer tanks. Since carbonates inhibit calcium phosphate precipitation, they are removed in a cascade stripper before the wastewater flow enters the Crystalactor®. The carbonate stripping occurs as pH is adjusted to 3.5 with H_2SO_4 (96%) (Gaastra *et al.*, 1998). The Crystalactor® consists of a cylindrical fluidized bed reactor (Figure 8) in which filter sand is used as seed material. The stripped wastewater is pumped through the reactor in an upward direction, and at such a high velocity (40-100 $m.h^{-1}$) the pellet bed is kept in a fluidized state.

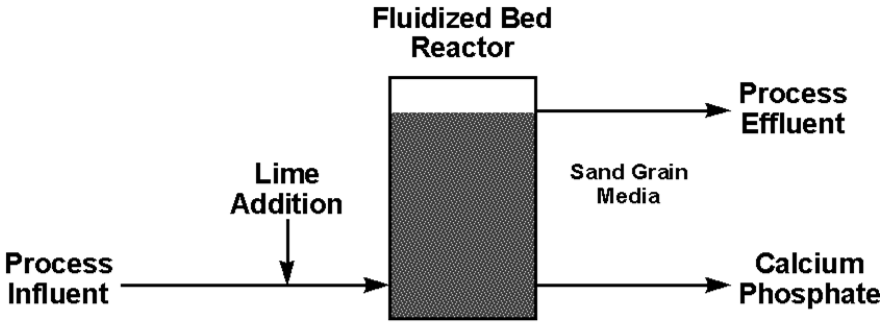

Figure 8 The Crystalactor® process flow diagram.

Efficient calcium phosphate crystallization requires a pH of 9. Therefore, $Ca(OH)_2$ solution is added to the reactor and the dosage is controlled by pH measurement. By adding $Ca(OH)_2$ and controlling alkalinity, calcium phosphate crystallizes on the nuclei (= sand). As the pellets grow in size and mass, they sink to the bottom of the reactor. At regular intervals, a

quantity of the largest fluidized pellets is discharged at full operation from the reactor and fresh seed material is added (Giesen and van der Molen, 1996). By selecting the appropriate process conditions, co-crystallisation of impurities is minimised and high-purity phosphate crystals are obtained (Giesen, 1999). The recovery rate can reach 70-80% of PO_4-P (Cornel and Schaum 2009).

In 1988 the first full-scale application for phosphate recovery was realized at the municipal wastewater treatment plant of Westerbork, The Netherlands. The plant operated successfully and removed phosphate below 1 $mg.L^{-1}$ P from the effluent of the biological section. No sludge was produced and the pellets were reused by the phosphate processing industry. Since phosphate free detergents were introduced in Dutch households, the phosphate concentration in raw municipal wastewater decreased significantly. Direct phosphate removal from the effluent by the Crystalactor® was thus not economically attractive anymore and the plant was closed (Giesen, 1999). In 1993 two full-scale demonstration plants applying this process for the treatment of municipal wastewater were built in Geestmerambacht (The Netherlands, 230.000 p.e.) and Heemstede (The Netherlands, 35.000 p.e.) (Piekema and Giesen, 2001). In 2011, the only operational Crystalactor® application was the one located in Geestmerambacht, the Netherlands, at one of the WWTPs of the Waterboard Uitwaterende Sluizen (Haarhuis, 2011).

The calcium phosphate Crystalactor® plant at Geestmerambacht produces 200 – 300 tonnes per year of phosphate pellets (13% P) (Wilsenach and van Loosdrecht, 2002). The produced pellets were first used in the production of chicken fodder (Gaastra *et al.*, 1998) and later as secondary raw material at Thermphos (Haarhuis, 2011). The Crystalactor® process has not become popular due to carbon dioxide stripping, the high operational pH to achieve precipitation, complexity of the process, the overdosing of calcium ions and high investment costs.

4.5. Phosphorus recovery from sewage sludge

4.5.1. Airprex®

The AirPrex® technology was developed and patented by the Berliner Wasserbetriebe after massive incrustations were found in the sludge dewatering lines of some WWTPs, downstream of anaerobic sludge digestion. This resulted in blockage of pipes and damage to pumps. Analyses of the incrustations showed that the precipitated material was mainly struvite with small portions of calcium phosphate (Heinzmann and Engel, 2006). The problem was solved by developing a method for controlled precipitation of struvite.

In the AirPrex® technology (Figure 9), the digested sludge is led through a cylindrical reactor, with an inner cylindrical zone mixed by air upflow and a settling zone between this inner cylinder and the outer cylinder. Due to the air bubbles the sludge is lifted upwards in the aerated zone in the middle of the reactor. After reaching the surface, the sludge settles in the tranquil zone in the outer part of the reactor. Ammonium ions (NH_4^+) and phosphate ions (PO_4^{3-}) are present in sufficient concentrations in the digested sludge, and magnesium ions (Mg^{2+}) are added as magnesium chloride ($MgCl_2$) to the reactor. Air is applied for two reasons. Firstly, it increases the pH by stripping CO_2 from the digested sludge.

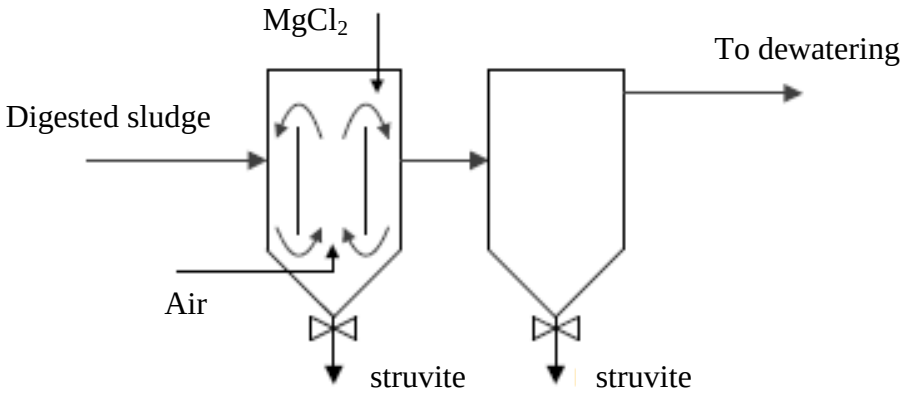

Figure 9 Schematic overview of the AirPrex technology (modified from Heinzmann, 2009).

Secondly, the internal recycle allows the struvite crystals to grow, until they reach a size at which they can escape from the recycle flow and settle. In a second tank, smaller

struvite crystals are also allowed to settle.

Struvite is continuously removed from the bottom of the 2 tanks. Sand washing equipment was tested and adapted to ensure cleaning and purification of the recovered struvite. This enables organic contamination in the recovered struvite to be reduced to less than 0.5 % TOC/mass (CEEP, 2012c). It was also observed that the reduction of phosphate ions and the increase of the bivalent metal ion, by the addition of $MgCl_2$ to the sludge, reduced the sludge water absorbing capacities. This leads to a stable, less hydrous floc and usually in 3 % higher dewatering rates (Veltman, 2012). This results in smaller sludge volumes and hence to lower transportation and disposal costs and is therefore an important economical incentive. Additionally, the dosing of cationic flocculants is reduced, as well as the need for anti-deposit agents.

Since 2006, P.C.S. GmbH, Hamburg, is the exclusive holder of the license for marketing of the process and the reactor. It has transferred this right to the SH+E GROUP, which also has the exclusive right to build AirPrex® systems. At the moment, three full scale plants are operational, one in Mönchengladbach (Germany), one in Waβmansdorf (Germany) and one in Emmen (the Netherlands). In these plants 80-90 % of the phosphate is removed from the liquid phase of the digested sludge as struvite.

The recovered struvite quality is conform, except for the water solubility, to the German fertilizer regulations and was certified in 2008 as mineral P fertilizer (Kern, 2009). The recovered struvite can therefore be marketed as a fertilizer. Berlin Wasserbetriebe is marketing the recovered struvite locally under the trade name of "*Berliner Pflanze*" (Berlin Plant) through cooperation with the fertilizer industry and distributors (CEEP, 2012c).

4.5.2. Seaborne

The Seaborne process was developed by the Seaborne Environmental Research Laboratory and treats municipal digested sewage sludge, to enable recovery of phosphorus and nitrogen, heavy metal separation, and energy recovery through incineration of solids (Seaborne, 2007). In the Seaborne process, nutrients are separated from the sewage sludge and processed to a fertilizer containing no heavy metals or organic pollutants (Müller *et al.*, 2005). In the first process step (Figure 10), an acidification of the sludge occurs by the addition of sulphuric acid in order to dissolve the solids and to release heavy metals and nutrients. The remaining solids are separated from the flow by using a centrifuge and a filter system and are then dried and directed to the sludge incineration. In the next treatment step, the sulphur-rich digester gas is used to precipitate the heavy metals from the effluent liquor. This consequently reduces the sulphur content of the digester gas and thus improves its value for energy production. In this case it is utilized in a co-generation plant.

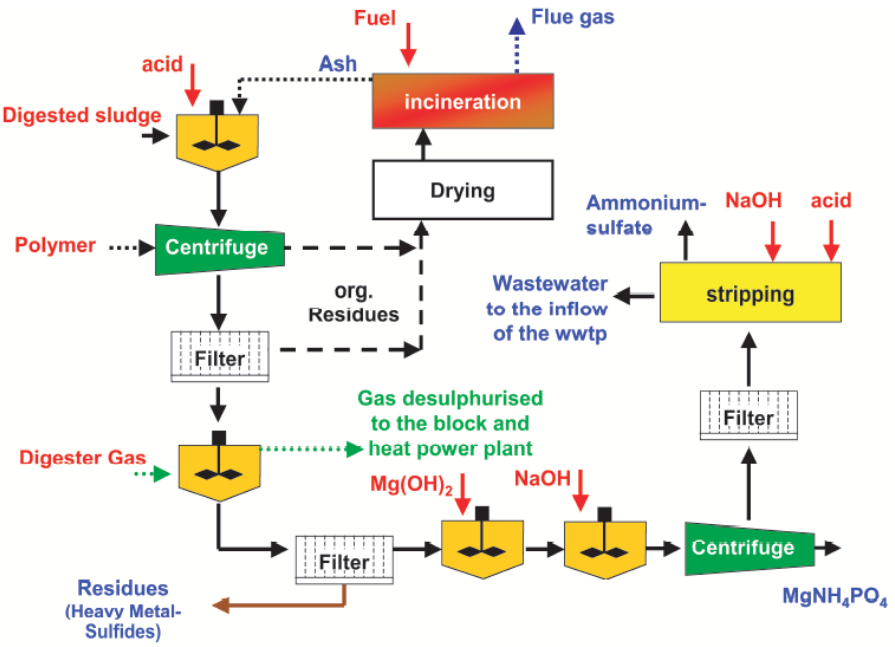

Figure 10 Process flow sheet of the Seaborne process at the WWTP Gifhorn (Müller *et al.*, 2005).

In the following process step the nutrients are recycled. Phosphate is precipitated as struvite by the addition of sodium hydroxide, to obtain an alkaline pH-value, and magnesium oxide as precipitant. Finally, the surplus nitrogen is recovered by air stripping of ammonia, followed by the production of ammonium sulphate with sulphuric acid. The treated process stream flows back to the influent of the WWTP.

The products of the Seaborne process struvite and ammonium sulphate, can be reused as fertilizer in agriculture (Günther *et al.*, 2008). A first full scale pilot plant was built between 2005 and 2006 at the wastewater treatment plant Gifhorn, (50,000 PE) in lower Saxony (Germany). It was estimated that around 90% of the nutrients (P, N) could be recovered by the Seaborne process, the phosphorus as struvite, the nitrogen for just under a third in struvite and the remainder in ammonium sulphate. This results in daily production of around 580 kg of struvite and 1300 kg of 41% ammonium sulphate solution. (CEEP, 2012b).

4.6. Phosphorus recovery from sewage sludge ash

Phosphorus that is not recovered from the liquid phase is present in the sewage sludge. The sludge produced sometimes ends up in landfills or in incinerators. Incineration of sludge reduces the volume by eliminating the organic content. The incineration residues are ashes which contain the nutrients and the inorganic material. Of the nutrients in the ash, phosphorus is the most important to recover. Since the untreated incineration ashes still contain heavy metal compounds above the legal limits and the phosphorus exhibits low bioavailability, they cannot be used in agriculture. There are two types of recovery methods of phosphorus from incineration ash: a dry thermal process and a wet chemical process (Kaikake *et al.*, 2009). For the wet chemical process, phosphorus is extracted by acid or an organic solvent and subsequently recovered from the solution. For the dry process, phosphorus is recovered by melting the ash. Incinerated ash can also be used as secondary material in the phosphate

industry for the production of elementary (white) phosphorus (Schipper *et al.* 2001). Until now, only two thermal processes are running full scale.

The remaining ash (after P-recovery) can be mixed with cement or concrete. Bricks or some other objects can be made of ash or the ash can be melted and solidified as a ceramic material (Levlin, 1999).

4.6.1. Thermochemical process: Ash Dec® (Outotec)

ASH DEC® Umwelt AG has developed and patented (2009) a thermochemical process to eliminate heavy metals from ash and simultaneously make nutrients plant available. Since 2011, the registered brand ASH DEC® has been acquired by Outotec (Hermann, 2012a).

A schematic overview of the process is given in Figure 11. Mono-incineration of the sludge completely destroys the organic pollutants in the first step. The incineration residues are ashes with high phosphorus content, but still contain heavy metal compounds above the legal limits for agricultural use (Adam *et al.*, 2009). In the second step, the thermochemical step, the sewage sludge ash is mixed with solid chlorine donors ($MgCl_2$ and $CaCl_2$) and exposed for 20-30 minutes to a temperature of 1000°C. At this temperature, heavy metals – usually mercury, cadmium, lead, copper and zinc - react with the salts, become gaseous and evaporate.

The amount of added chlorine donors depends on the concentration of heavy metals in the ash and the target removal rates as required by national fertilizer legislation in European countries (Hermann, 2009a). Additionally to the removal of heavy metals, new phosphate mineral phases (so called calcined phosphates) are built up during the thermochemical process resulting in an improved P-bioavailability. The P-mineral phases (calcined phosphates) that are formed at temperatures of approximately 1000 °C are the calcium phosphate chlorapatite ($Ca_5(PO_4)_3Cl_{1-x}(OH)_x$), the magnesium phosphate farringtonite ($Mg_3(PO_4)_2$) and the calcium-

/magnesium phosphate stanfieldite ($Ca_4Mg_5(PO_4)_6$). So due to the thermal treatment process, the formation of the Mg-bearing mineral phosphate phases stanfieldite and farringtonite was found to be the reason for the improved bioavailability of phosphorus in the treated ashes (Adam *et al.*, 2009; Adam, 2009).

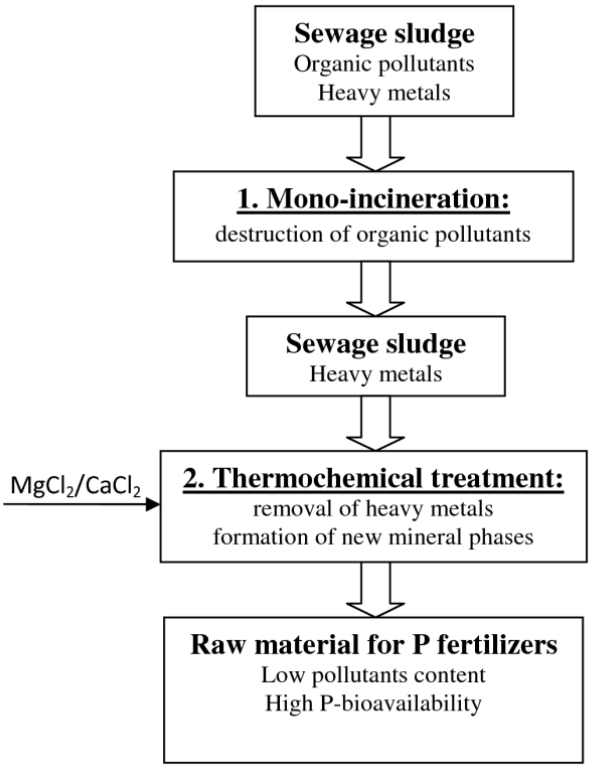

Figure 11 Schematic overview of the Ash Dec® process (modified from Adam *et al.*, 2009).

A 200 $kg.h^{-1}$ pilot plant was successfully operated in Leoben, Austria (by ASH DEC Umwelt AG, and now by Outotec GmbH) and an industrial scale plant is currently being planned by Outotec GmbH (CEEP, 2011).

After the thermochemical treatment, the treated ashes are mixed with other nutrients (NH_4NO_3, K_2SO_4, KCl) and the mixtures are pelletized using special mixers. In this way the ASH DEC NPK-fertilizer (20-5-8 as $N\text{-}P_2O_5\text{-}K_2O$) is produced and currently sold under the PhosKraft® brand (Hermann, 2009b; Adam, 2009). They contain two orders of magnitude

less cadmium and one order of magnitude less uranium than most phosphate rock based fertilizers and are equally effective in terms of yield and phosphate uptake by crops. The product matches the principles of organic farming and is at present under scrutiny for being admitted in Annex II A of Regulation (EC) 889/2008 (Hermann, 2012b), as a plant protection product. Leading soil and plant nutrition research institutes in Germany, Switzerland, The Netherlands and Austria have tested and confirmed the product quality in numerous pot and field tests. As a consequence, Austrian and German governments have licensed PhosKraft® fertilizers for application on pasture and cropland (Hermann, 2012b).

4.6.2. Electrothermal phosphorus recovery

Thermphos International, located in Vlissingen (the Netherlands) is one of the world's largest producers of phosphorus, phosphoric acid, phosphates, phosphonates and phosphorus derivatives. They are even the only white phosphorus producer in Western Europe. To make white phosphorus Thermphos relies on phosphate rock. For the production of white phosphorus, an electrothermal process is applied. On a yearly base 600 000 tons of phosphate rock (approximately 90 000 tons of phosphorus) is bought all over the world (Korving and Schipper, 2007). As phosphate rock is a finite resource, the company has decided to replace a part of their phosphorus intake (17500 tons P) by recovered materials (Schipper *et al.*, 2001). Therefore Thermphos concluded a cooperation with the Sewage sludge incineration plant of Noord-Brabant (SNB) from 2007 to 2012. SNB is the largest sludge incineration plant in Europe, located in Moerdijk, the southern part of the Netherlands. During this five year cooperation SNB supplied phosphate rich sludge ash to Thermphos, that uses this sludge ash in its production process.

An important condition for the sludge ash is that it contains low iron concentrations and high phosphorus concentrations. It is important that the molar ratio of Fe/P is lower than

0.3 (Geeraats and Reitsma, 2007) because during the process iron reacts in the ash and forms a byproduct ferrophosphorus. A high iron content thus leads to a decrease of the conversion of phosphorus and an increase of the byproduct ferrophosphorus which is not desired (Geeraats and Rieitsma, 2007). Table 6 represents the requirements for the phosphorus content as well as the most important substances disturbing the electrothermal process: copper, zinc and iron. As described earlier, the produced calcium phosphate from the Crystalactor® of Geesterambacht was used in the production process of Thermphos. In Table 6 the quality of the precipitate from that plant is compared with the P-industry requirements (Schipper *et al.*, 2001). It can be concluded that the calcium phosphate from the Crystalactor® can be used by the phosphorus industry without limitation.

Table 6 Quality of calcium phosphate precipitation compared with the requirements of the phosphorus industry (Thermphos) for sewage sludge ash (Schipper *et al.*, 2001).

Element	**Concentrations required by the phosphorus industry (g.kg^{-1} ash)**	**Calcium phosphate from the Crystalactor® (g.kg^{-1} ash)**
P_2O_5	> 250	260
Copper	< 0.5	0,0016
Zinc	< 0. 1	0,035
Iron	< 10	-

Recovery of phosphorus from ash does not require major changes at the WWTP, although changing from iron precipitants to aluminum or calcium precipitants would be a better option for better recyclability (Schipper *et al.*, 2001). Nitrogen present in recovered materials causes a serious emission or gas scrubbing problem in the sintering stage, since NH_3 will be volatilised. Therefore, struvite is not suitable for replacing raw material in

electrothermal process due to the ammonia content (Schipper *et al.*, 2001). To deal with this problem struvite could be decomposed according the following reaction (Bhuiyan *et al.*, 2008):

$$MgNH_4PO_4.6H_2O \rightarrow MgHPO_4 + NH3\uparrow + 6H_2O \quad (5)$$

It this way the volatized ammonia could be recuperated as $(NH_4)_2SO_4$ within an acid scrubber. The remaining $MgHPO_4$ could then be used as an alternative for phosphate rock.

5. Full scale technologies for P-recovery from livestock manure

Most of the phosphate recovery techniques are developed for industrial and municipal wastewater. At the moment only a few phosphate recovery techniques are developed for livestock manure treatment.

5.1. Final products from P-recovery (livestock manure)

K-struvite and calcium phosphate are two final products that are recovered from two different full scale installations. Calcium phosphate has already been discussed (4.2.1). K-struvite ($KMgPO_4.6H_2O$) has a similar structure as struvite ($MgNH_4PO_4.6H_2O$); the only difference is the replacement of NH_4^+ into a smaller K^+ ion. The solubility products (Ksp) of K-struvite and struvite have been reported by Taylor *et al.* (1963) and equals $2.4.10^{-11}$ and $7.1.10^{-14}$, respectively. From these solubility constants it can be concluded that if both ammonium and potassium are present in excess, struvite will precipitate instead of K-struvite. This means that K-struvite will only precipitate if the excess of potassium is much higher than ammonium. Therefore K-struvite can for instance be formed from denitrified wastewater (Schuiling and Andrade, 1999). Examples of potassium rich wastewaters are leachate, urine and livestock manure. Also K-struvite is not recognized as a fertilizer by the EU directive 2003/2003. This

impedes the marketing of the product.

5.2. Liquid swine manure treatment system developed by Vanotti *et al.* (2005)

Livestock manure is a mixture of urine, water and feces. Livestock urine usually contains more than 55% of the excreted N of which more than 70% is in the form of urea (Vanotti and Szogi, 2009). Hydrolysis of urea by the enzyme urease produces ammonium and carbonate according to the following reaction:

$$CO(NH_2)_2 + 2\ H_2O \rightarrow 2NH_4^+ + CO_3^{2-} \quad (6)$$

Consequently, precipitation of phosphate in animal wastewater using an alkaline compound such as lime is very difficult due to the inherent high buffering capacity of liquid manure. This problem can however be solved by using a pre-nitrification step that reduces the concentration of both ammonium (Equation 7) and bicarbonate alkalinity (Equation 8) (Vanotti *et al.*, 2005):

$$NH_4^+ + 2\ O_2 \rightarrow NO_3^- + 2H^+ + H_2O \quad (7)$$

$$HCO_3^- + H^+ \rightarrow CO_2 + H_2O \quad (8)$$

The buffering effect of ammonium is reduced by biological nitrification of ammonium to nitrate (Equation 7). Simultaneously, the buffering effect of bicarbonate is greatly reduced with the acid produced during nitrification (Equation 7 and Equation 8). These two simultaneous reactions leave a less buffered liquid. In this way smaller amounts of lime have to be added to the wastewater to recover the phosphate as calcium phosphate.

Based on the previous background Vanotti *et al.* (2009) developed a patented process (2010) to recover phosphate from liquid swine manure. In the treatment system (Vanotti *et al.*, 2003; Vanotti *et al.*, 2005; Szogi and Vanotti, 2009) raw liquid swine manure is first treated through an enhanced solid-liquid separation process with polymers to remove most of the carbonaceous material from the wastewater. The liquid swine manure is then treated with the

nitrification to oxidize ammonium to nitrate. The latter also reduces the buffer capacity of the wastewater. The pH of the nitrified wastewater is then increased by the addition of calcium hydroxide which results in the precipitation of calcium phosphate. The phosphate precipitate is separated from the wastewater by a phosphorus separation unit (Vanotti *et al.*, 2007). A denitrification tank can also be incorporated into the treatment system to provide total N removal in addition to the phosphate removal. The effectiveness of the technology was tested in a pilot field study at ten swine farms in North Carolina, where 95-98% of the P was precipitated from the anaerobic lagoon effluent. The first full demonstration plant was installed on Goshen Ridge farm in North Carolina and was evaluated during one year. Phosphate removal efficiencies of 94 % were obtained during this test (Vanotti *et al.*, 2007). The final product is a calcium phosphate rich sludge that can be used as P fertilizer (Bauer *et al.*, 2007).

5.3. Calf manure treatment in Putten (the Netherlands)

A full scale plant for the recovery of K-struvite from calf manure has been installed at Putten (the Netherlands) (Schuiling and Andrade, 1999). This facility treats 115 000 m^3 calf manure per year (Schuiling and Andrade, 1999).

Before the phosphate is recovered as K-struvite, the calf manure is separated in a solid and a liquid fraction. The liquid fraction is then processed in a biological activated sludge system, in which the organic carbon and the nitrogen are broken down. After nitrification/denitrification and settling, the phosphate rich effluent is treated with a magnesium source (MgO) to form K-struvite in a series of three continuously stirred tanks. Mechanical mixers keep solids in suspension, mix the liquor to bring ions in contact with nuclei and to dissolve MgO, which is rather poorly soluble. The dissolving MgO increases alkalinity to pH of 8.5 - 9, where K-struvite starts to precipitate (Schuiling and Andrade,

1999). After K-struvite precipitation the effluent goes to a lamellae separator. The clarified effluent contains between 15 -25 mg.L^{-1} P (95% removal efficiency) (Reitsma and Bults, 2006).

Approximately 125 kg P is recovered per day. Although potassium removal or recovery is not a priority in wastewater treatment, it is a valuable fertilizer component (Wilsenach and van Loosdrecht, 2002). The obtained K-struvite is not recognized by the EU legislation as a fertilizer. Therefore it cannot be sold or transported as a fertilizer and therefore the market for K-struvite is rather small. K-struvite can be used as a material for fertilizers or as secondary raw material for the phosphate processing industry. However, the latter is difficult for low production quantities (tons per year) (Verhoek, 2011). In the case of Putten the K-struvite is transported and processed by Thermphos (Reitsma and Bults, 2006).

6. Discussion

6.1. Recovery from the liquid phase versus recovery from the sludge/sludge ash

Compared to the wet-chemical process (e.g., Seaborne) and the thermal processes (e.g., Thermphos and Ash dec®), precipitation from the liquid phase (e.g., Phospaq™, NuReSys®, ANPHOS®, Phosnix and Pearl™) is a simple process. About 40-50 % of the phosphate (of WWTP influent) can be recycled by adding a magnesium or calcium compound as the precipitant and NaOH or CO_2 stripping for increasing the pH. In this way struvite or calcium phosphate can be precipitated from the liquid phase in a stirred tank reactor or fluidized bed reactor. Stirred tank reactors are simple in operation when compared to fluidized bed reactors (Stratful *et al.*, 2004). The operation of fluidized bed reactors require high flow rates and/or significant mixing energy to ensure that the bed of seeds is continuously fluidized which will lead to a higher energy consumption compared to stirred tank reactors.

Several techniques have been developed for phosphate recovery as calcium phosphate, but only a few have been practically used at full scale, since the existing techniques are far from perfect and economical. The DHV Crystalactor® is an example of a full scale phosphate recovery process for calcium phosphate. There are some strict conditions for the influent of this process: before the influent enters the fluidized bed, it must be acidified to pH 3 to remove carbonate and then be alkalised to pH 9 to realize the crystallization of calcium phosphate. The need for carbon dioxide stripping and the high operational pH to achieve precipitation, obviously consumes a lot of energy and chemicals. This correspondingly increases the cost of the technology. Besides that, sand is added to the crystallization reactor since calcium phosphate crystallites aggregate around existing surfaces (heterogeneous nucleation) rather than growing spontaneously from the solution (homogeneous nucleation), as it is the case for struvite. Vanotti *et al.* (2009) proved that the problem of the carbonate interference can be circumvented by treating the wastewater in a nitrification step before precipitating phosphate as calcium phosphate by the addition of lime. Struvite precipitation is more applied at full scale than calcium phosphate precipitation, this can be mainly explained by the more simple operation and easier crystallization.

When recovering P from the sludge, as in the AirPrex technology, one has to take into account that the crystals formed will have to be washed. In the case of the AirPrex technology, a sand washing equipment was used for cleaning and purification of the recovered phosphate, resulting in an additional investment cost.

Recovering phosphorus by wet-chemical and thermal processes from the sludge/sludge ash can obtain higher P-recovery rates than recovering phosphorus from the liquid phase. Up to 90 % of the phosphorus can be recovered from sludge and sludge ash, but large amounts of chemicals and/or energy and many process steps are required, which mean that these processes have high investment and operational costs.

6.2. P-recovery processes: field of application

Recycling P from the liquid phase can be done on a small or a large scale and at nearly every WWTP. The suppliers of the techniques for P recycling from the liquid phase, state that these processes can be applied for wastewater treatment in the agricultural dairy, brewery and starch manufacturing industries, potato processing companies, rejection water (Colsen, 2009), manure treatment and urine (Kampschreur, 2011). However, up till now these processes are only used in a few potato processing companies and for the treatment of rejection water. Potato processing companies are suitable for phosphate recovery since their wastewater contains large amounts of phosphate. During preparation of the pre-baked frozen product, the potatoes are treated with sodium acid pyrophosphate after the blanching treatment. Sodium acid pyrophosphate ($Na_2H_2P_2O_7$) is needed to complex iron (Fe^{2+}). In this way sodium acid pyrophosphate prevents that iron in the potato reacts with chlorogenic acid during the heating processes (Rossell, 2001). The oxidation of the Fe^{2+}-chlorogenic acid complex by oxygen from the air would otherwise result into a grayish colored substance that causes the so-called 'after-cooking' grey discoloration (Rossell, 2001). The blanching treatment also causes leaching of phoshate from the potatoes. As such, the blanching treatment and the addition of sodium acid pyrophosphate are the main reasons for the high phosphate concentrations in the wastewater of potato processing companies. Agricultural diary, brewery and starch manufacturing industries have less phosphorus in their wastewater and therefore the operational cost to recover phosphate as struvite will be more expensive. One must also consider that the production of struvite in different smaller reactors over the different companies may result in a variation in the struvite quality. Also the low production quantities in those companies can have a negative effect on the selling price of the struvite. The production of larger quantities of struvite with the same quality would result in a better price and a better market for struvite.

Manure and urine contain large nutrient concentrations which makes the recovery of phosphate as struvite more interesting. According to Larsen and Gujer (1996), 75 % of the total N load and 50 % of the total P load in municipal wastewater originate from urine. However, the collection systems of municipal wastewater use considerable amounts of greywater, flush water and even stormwater. As a consequence of this dilute nature of municipal wastewater, the recovery of N and P is economically and energetically more expensive than recovering it from undiluted wastewater. Separate urine collection would largely improve the potential for nutrient recovery, because the concentrations of N and P would be a hundred times higher than in municipal wastewater (Wilsenach and van Loosdrecht, 2002). Also manure contains large P concentration, however research showed that it is more difficult to obtain large crystals (Wilsenach *et al.*, 2007; Ronteltap *et al.*, 2010). Further research on the removal of phosphorus from urine and manure is thus necessary since it has a large potential of recovering phosphate as struvite.

Recycling P from the sludge or sludge ash with the wet-chemical process requires fermentation of the sludge, which is not economically feasible on a small scale. Both the thermal treatment plants and incineration are large-scale processes, not operating at the site of a WWTP. In general, incinerators that combust sewage sludge, meat and bone meal, digestion residues from biogas facilities and similar material with usually no or little co-combustion of industrial residues produce ashes that are suitable for nutrient recovery to produce fertilizers with the thermal treatment process. Preferred plant locations are close to incinerators of reasonable combustion capacity. It could be a good technology in highly industrialised countries where laws prohibit the use of treated sewage sludge in agriculture, helping to close the P cycle.

6.3. Plant availability of the recovered struvite

Johnston and Richards (2003) evaluated eleven recovered and lab synthesised struvite samples as a source of phosphorus and compared them with monocalcium phosphate (MCP) for the availability of plant growth. In their test, soils with pH 6.6 and 7.1 and with Olsen P content of 28 and 11 $mg.L^{-1}$, respectively, were used to grow perennial ryegrass. All the struvite samples were sieved by a 0.5 mm sieve. Results indicate that the recovered struvite samples did not have significant difference between themselves or to MCP in view of the phosphate offtakes by the ryegrass. However, a slight difference in the yields of ryegrass was indeed found: the ryegrass by using the recovered struvites had smaller dry-matter yields than those of using the synthetic struvites. The authors attributed this slight difference to the struvite crystal size. The conclusion of this investigation supports to use struvite as a potential fertilizer. The authors also suggest to produce struvite with crystal size of 2 – 4 mm, which allows to be spread by farm equipment.

Bauer et al. (2007) investigated the effect of recovered struvite size on phosphate plant availability. The work confirmed that recovered struvite is suitable for fertilizer use and it was found that over 99% of P in the recovered struvite samples was plant available. The work also found that the struvite size of 0.5 – 1.0 mm is suitable for a readily available fertilizer; while the size of 2.0 – 4.0 mm struvite may be used as a slow released fertilizer.

6.4. Influence of legislation, national policies on the implementation of P-recovery technologies.

Up till now, there are no international strategies for sustainable phosphorus recovery and reuse in the context of food security (Cordell *et al.*, 2009). On the other hand nation contexts and drivers differ from region to region. This explains the wide variety in P-recovery technologies and the fact that full scale P-recovery processes are not yet widely spread all

over the world. Full scale installations are operational in some countries in Europe (the Netherlands, Belgium, Germany, Austria), North America and Asia (Japan). The implementation of those technologies was strongly influenced by national regulations and/or the presence of industrial facilities which can use recovered phosphorus. In the Netherlands, for instance, the national regulations governing the maximum heavy metal content of the sludges from WWTP going to agricultural are among the most severe in Europe. Therefore, the Netherlands are one of the pioneers of the developing of P-recovery technologies, starting with the DHV crystalactor®, followed by struvite precipitation with PHOSPAQ® and ANPHOS®. However, P requirements in the soils are weak and largely met by spreading animal waste and mineral fertilizers. In this way, the P-recovery as fertilizer (like struvite) is not promoted. Another consequence of these stringent national requirements is the massive use of incineration (around 60% according to Roeleveld *et al.*, 2004). In this way, the presence of the company Thermphos International favoured the recycling of phosphorus from sludge ashes in the P-industry since 2007.

The situation in Belgium is likewise. Prayon, one of the world leaders in the phosphate sector, has one location in Belgium. It manufactures an extensive range of phosphate and fluorine products that are used in food applications, industrial applications, fertilizers and other applications such as pharmaceuticals. They also have the intention of using recycled phosphate in their production process. The difference with Thermphos, using sludge with a low Fe/P, is that Prayon needs 100% calcium phosphate, without sludge (personal communication). This is less interesting since no company in Belgium recovers phosphate as calcium phosphate at full scale.

Sweden also has stringent national requirements on the spreading of sludge to agriculture land. Besides that, the Swedish Environmental Protection Agency (SEPA) has proposed an intermediate target for P-recycling that by 2015, at least 60 % of the phosphorus

in wastewater should be restored to productive soil, of which half should be returned to arable land (Stark, 2007). In order to reach these objectives, the choice of techniques and the strategy of recovery are very specific to the national context. Since a recovery of more than 50 % is required, technologies will focus on the recovery of P from sewage sludge rather than from P-recovery from the liquid phase. Requirements of both efficient phosphorus removal and recovery have led to reconsideration of present wastewater and sludge treatment in Sweden. Systems are being developed (KREPRO, Cambi/KREPRO and BioCon) which have the possibilities to recover phosphorus with iron precipitation (Hultman *et al.*, 2001). Afterwards the sludge has to be incinerated and the phosphate products are extracted with acid and/or heat.

In Switzerland, the protection of the environment and more precisely the fight against risks of eutrophication of surface water are an integral part of the objectives of the Swiss Federal Republic. The regulatory limit for wastewater discharge in Switzerland is 0.8 $mgP.L^{-1}$ (Lee *et al.*, 2009). In order to reach such results the physicochemical P-removal (mainly with iron salts) has been preferred to the biological P-removal and no P-recovery technologies are developed in this country.

The German Federal Environment Office (UBA) suggests recovery from sewage sludge and effluents (Stark, 2007). Since 2008 German fertilizer legislation (Düngemittelverordnung) allows the recycling of sewage sludge ash as fertilizer if concentration limits for pollutants are met (As, Pb, Hg, Cd) (Postma *et al.*, 2011).
In the other countries of Europe there is not a specific context motivating the P-recovery. Therefore the development of full scale P-recovery technologies are not yet found in those countries since it is not an national objective.

In the Japanese national context, the huge costs of sludge disposal, the dependence on phosphorus ore import and the prevention of eutrophication has orientated the decision of P-

recovery (Ueno and Fuji, 2001). Phosphate removal in the US has attracted the attention of inventors trying to recover phosphorus from sludge or sludge liquor to reduce the occurrence of pipe blockage in advanced wastewater facilities (Cordell *et al.*, 2011). In Canada, a British Colombia company has successfully implemented a phosphate recovery process, Pearl™ and has become market leader in the US.

6.5. Influence of legislation, national policies and certification on the market for the end products of P-recovery technologies.

An essential requisite for the recovery of phosphate from wastewater is obtaining a final product in large quantities with a constant quality, sufficient purity, free from pathogens and with the right physical properties. Outlets for phosphate containing end products such as struvite and calcium phosphate are very important to commercialize a phosphate recovery technology on large scale. With all the full scale phosphate recovery techniques it is possible to produce an end product that has a potential to be used as fertilizer or as secondary material for the fertilizer industry. With the controlled precipitation systems such as Phospaq™ and ANPHOS® the struvite obtained is a kind of slurry and after draining it has the structure of sand. This kind of struvite can be contaminated with organic substances and does not always has a homogeneous character. Struvite gained from controlled crystallization systems such as Pearl™, Phosnix and NuReSys® give a clean product that is easy to dry and has good product properties to be mixed with other fertilizers or can be used as fertilizer as such. Also the separation of pellets from the wastewater is easier in comparison with the separation of fine struvite crystals from a matrix of digested sludge in the case of the Airprex® system.

The legislation and national policies that determine the status of those end products in terms of market and use for agriculture can however be an inhibiting factor. Therefore the

facilitative role of the (national) governments is very important.

In Europe struvite is not yet recognized as fertilizer and therefore a special admission of the national government is necessary to obtain a status as fertilizer. If the special admission is not given by the national government, struvite is seen as a waste. Therefore, the distribution of the produced struvite as fertilizer in agriculture is often a bottleneck. Of the full scale techniques mentioned, only the struvite products of Pearl™ and NuReSys® (respectively Crystal Green® and BioSTRU®) are certified as fertilizers in US/UK and Belgium, respectively. The product of the Phosnix process in Japan is marketed as a mineral fertilizer for the cultivation of rice. The PhosKraft® fertilizer obtained with the thermochemical process Ash Dec® has been licensed by the Austrian and German governments. The struvite obtained with the Seaborne process is only used locally. It can be concluded that the produced end products are mostly used in the countries where they are produced and thus in most cases the market is very small. To establish a sustainable market for recycled phosphorus in Europe, support of the European Union is essential. That is why frontrunners (knowledge institutes, businesses, NGO's and governments) from several European Member States have decided to join forces with each other and the European Commission in organizing the first European Sustainable Phosphorus Conference (6-7 March 2013). At this conference, participants reached consensus to launch the European Phosphorus Platform to continue dialogues, raise awareness and trigger actions to address the Phosphorus Challenge that have implications for ensuring food security, geopolitical stability and environmental sustainability.

In America, Crystal Green® is regulated as a fertilizer product. Therefore it must meet the fertilizer registration requirements of the State where it is distributed.

6.6. Economic feasibility for struvite precipitation

P-recovery techniques have been widely studied and a number of full scale installations for P-recovery are already operational in Europe (the Netherlands, Belgium, Germany, Austria), North America and Asia (Japan), showing that P-recovery is technically feasible. However, contributions on the field of economic feasibility are much more limited (Jeanmaire and Evans, 2001; Shu *et al.*, 2006; Dockhorn, 2009; Molinos-Senate *et al.*, 2011). Schaum (2007) reported costs in a wide range of 2.2 to 8.8 EUR.kg^{-1} P depending on the process. More up to date information about the NuReSys® process operating in Belgium could be obtained (Moerman, 2012). The OPEX (Operating Expenditures) for the NuReSys® process treating 60 m³.h^{-1} wastewater, containing 120 mg.L^{-1} PO_4-P is 1.6 EUR.kg^{-1} P. The CAPEX (capital expenditures) of the process is 4.4 EUR.kg^{-1} P. The installation can be amortized during the first five years of operation for this specific case. For the removal of lower P concentrations both operational and investment costs will be higher. Struvite has a commercial value, either as a phosphorus fertilizer, or as a supplement to compost or other fertilizers. Dockhorn (2009) calculated the value of struvite based on its individual components (P, N and Mg^{2+}). So the price of a multicomponent fertilizer should equal the sum of the price for the individual components at equal product qualities. According to Dockhorn (2009) the same calculation was done based on the fertilizer prices of March 2012 (Table 7) and a market value of 684 EUR.ton^{-1} struvite was obtained, where 48 % was related to P, 7,6 % to N and 44,4 % to Mg^{2+}. Although the market value of this fertilizer is expected to be high (calculated market value of 684 EUR.ton^{-1} struvite or 2.6 EUR.kg^{-1} P), struvite is not currently a common commercial product that has a well-defined market value. The market value for struvite, obtained with NuReSys® process varies between 100 – 120 EUR.ton^{-1} struvite or 0.38 – 0.46 EUR.kg^{-1} P, taking into account that 48 % of the market value of struvite is related to P. Ideally, the sale of the struvite produced would cover all the costs or even generate profit.

Although economical feasibility is usually the main driving force for the implementation of a new technology, there are several other advantages related to the implementation of a P-recovery technology. The problem of undesired P-precipitation in the form of struvite can be diminished. P-recovery (as struvite) can result in a decrease of costs for the treatment and disposal of sludge. It was estimated that P-recovery in a WWTP would reduce the sludge production by 2-8 % dry matter (Jeanmaire and Evans, 2001). It also increases the availability of a non-renewable resource. According to Molinos-Senate *et al.* (2011) P-recovery becomes an economically feasible process if environmental benefits are also considered. One important environmental benefit is the prevention of eutrophication in the receiving environment. This means that phosphorus has to be removed from the wastewater anyway and that the operational cost of the conventional removal of phosphorus from wastewater must also be compared with the operational cost of P-recovery. The operational cost for conventional removal of phosphorus from wastewater varies between 5-10 EUR.kg P^{-1}. This includes the cost for $FeCl_3$ and the processing of the additional sludge it creates. In the case of the NuReSys® process, the sale of the struvite produced does not cover all the costs. However the main driving force for the implementation of this new technology should be that the operational cost of the P-recovery technology is less expensive compared to the operational cost of the traditional P removal process.

According to the World Bank, the price for rock phosphate was 34 EUR per metric ton (= 0.20-0.26 EUR.kg^{-1} P) in March 2007 and increased to 146 EUR per metric ton (= 0.83-1.12 EUR.kg^{-1} P) in March 2012 (World Bank, 2012).

In spite of the price increase, these values show that it is still cheaper for the fertilizer industry to use rock phosphate as feed stock. However if struvite is used directly to the land, the price becomes concurrently with the average cost of common fertilizers (Table 7). Fertilizer prices paid by farmers (retail prices) are reported by USDA and are available on its website in a

monthly report entitled Agricultural Prices (USDA, 2012). The price that farmers pay for phosphorus varies from 1.9 to 3.3 EUR.kg^{-1} P (Table 7). Compared with the operational cost of 1.6 EUR.kg^{-1} P for the NuReSys® process (treating 60 m^3.h^{-1} wastewater containing 120 mg.L^{-1} PO_4-P) it can be concluded that if the market for struvite would be more specified and stimulated by research and government, the market value of struvite could increased to a price that covers the operational costs of the P-recovery technology. In this way P-recovery techniques would be even more beneficial.

Table 7 Total average cost (EUR.kg^{-1} P; March 2012) of diammonium phosphate and super phosphate fertilizers at farm (USDA, 2012).

Product	**Price (EUR.ton^{-1})**	**Price (EUR.kg^{-1} P)**	**Price (EUR.kg^{-1} N)**	**Price (EUR.kg^{-1} Mg^{2+})**
Diammonium phosphate	544	1.9	0.92	-
Super phosphate (45 % phosphate)	498	3.3	-	-
Urea	415	-	0.90	-
Nitrogen solutions (30 %)	280	-	0.93	-
Magnesium (metal)	3100	-	-	3.1

The largest operational cost for struvite precipitation is related to the cost for the addition of a magnesium source (Dockhorn, 2009). Therefore, benefits of struvite recovery could be significantly improved if a waste material from the magnesium industry would be used as a magnesium source. Magnesium hydroxide or magnesium chloride purchase costs are then

avoided and overall resource recycling is further improved. This strategy was successfully tested at laboratory scale in Spain (Quintana *et al.*, 2008). Another example of a cheap magnesium source could be seawater.

When there is no economical driving force, regulations can also be a stimulating factor, as discussed in the previous section.

6.7. Phosphorus recovery: future perspectives

In this review a variety of different approaches are described to recover phosphorus from wastewater, sludge and sludge ash. According to a survey of experts in the field of phosphorus recovery (Satorius *et al.*, 2012), simple techniques such as the precipitation of phosphate from the liquid phase (e.g., sludge liquor) seem to be preferred. So the experts appeared to prefer less costly approaches even at the expense of lower yields. However, if the sewage sludge is or has to be incinerated before the deposition of its ash in landfills (obligatory in Switzerland, the Netherlands, Austria and Germany), then phosphorus recycling from ash becomes more interesting and has to be considered. In that case, the high cost of incineration is not assigned to the recovery of phosphorus. Sewage sludge ash can also be used as a substitute for phosphate rock in the process of Thermphos. This process needs iron free ash (Fe:P < 0.3) as input. Therefore, aluminium salts are proposed as an alternative to precipitate phosphate from the wastewater. However, experts in the field of phosphorus recovery are not sure about the acceptability of this approach because it is sometimes not socially accepted in the context of food production (Satorius *et al.*, 2012).

Linderholm *et al.* (2012) examined the life cycle assessment (LCA) of phosphorus alternatives such as certified Swedish sewage sludge, struvite precipitated from wastewater (Pearl™) and phosphorus recovered from sludge incineration (ASH DEC®) and compared it with the LCA of the mineral fertilizer triple superphosphate (TSP). In the LCA study, the

impact of global warming, eutrophication, energy demand and cadmium flows to farmland were considered. The use of sewage sludge to farmland was the most efficient option in terms of energy and greenhouse gas emissions, but added most cadmium to the soil. This confirms the increasing contamination of phosphorus containing waste sludge with heavy metals next to the presence of toxic organic substances. Therefore, its application in agriculture will become increasingly unpopular because of the growing awareness of environmental and health issues. This will probably result in the phase out of the direct use of sludge to farmland in many countries. As a consequence the use of phosphorus recovery techniques will increase in the future. Struvite precipitated from wastewater resulted in less greenhouse gas emission than the mineral fertilizer TSP but is more energy demanding. In that case, the use of alternative energy would be beneficial if struvite is precipitated from wastewater. Phosphorus recovered from incinerated sludge was the most energy demanding option and gave most emissions of greenhouse gases.

7. Conclusions

Phosphorus is a growth limiting nutrient that is mined from rock ore, refined, used in fertilizers, and discharged to the environment through municipal and industrial sewage. The impacts of phosphorus discharge include severe eutrophication of fresh water bodies as well as irreplaceable loss of a valuable nutrient. The sustainable use of phosphorus must include recovery of phosphorus from municipal wastewater, industrial wastewater, livestock manure and urine and subsequently using it as a fertilizer or reprocessing it as a fertilizer.

P-recovery has been widely studied and a number of full scale installations for P-recovery are already operational in Europe (the Netherlands, Belgium, Germany, Austria), North America and Asia (Japan), showing that P-recovery is technically feasible. However the economical feasibility, legislation and national policies have an influence on the

implementation of a technically feasible technology. Phosphate can be recovered from the liquid phase, sludge phase or from ash of a wastewater treatment plant. About 40-50 % of the phosphorus can be recovered from the liquid phase, while 80- 90 % can be recovered from the sludge phase or the sludge ash. P-recovery from the liquid phase is a simple process, whereas P-recovery from the sewage sludge ash have a higher energy consumption and higher investment cost. The most appropriate way of recovering P in a given country will differ from region to region since national context and drivers are different. Therefore it is likely that not just one social-technical solution will meet all the needs. The international and national governments play a very important role in creating a sustainable market for recycled phosphate products Therefore stimulation of the recovery processes by the governments and a revision of the fertilizer regulation (for Europe) is necessary.

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